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Development of New Addition-Type Composite Resins

ORIGINAL

R. J. Kray

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Development of New Addition-Type Composite Resins

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CIBA-GEIGY Corporation
Ardsley, New York

Prepared for
Langley Research Center
under Contract NAS1-13703

National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1981

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FOREWORD

The work was performed at the Ardsley Plastics and Additives Research Laboratories of CIBA-GEIGY Corporation by Dr. R. J. Kray, principal investigator with the assistance of Messrs. A. Ferrara and P. Clarke.

The author is indebted to Mr. R. Coulehan who conducted physical tests and Dr. E. Catsiff who carried out polymer characterizations. The assistance of various members of the Corporate Analytical Department is also appreciated.

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U. S. Customary to SI Conversions

°F	°C
50	10
77	25
120	49
140	60
150	66
158	70
160	71
194	90
200	93
212	100
221	104
230	110
239	115
248	120
250	121
257	125
275	135
300	149
311	155
320	160
325	163
338	170
350	177
370	188
375	191
390	199
400	204

°F	°C
420	216
425	219
435	224
440	227
450	232
460	238
465	241
475	246
487	253
490	254
498	258
500	260
509	265
525	274
540	282
545	285
550	288
561	294
572	300
575	302
600	316
621	328
669	354
743	395
765	407
775	413

psi	MPa
100	0.7
200	1.4
300	2.1
400	2.8
600	4.2

Inches	Millimeters
1/8	3
1/4	6
1/2	13
5/8	16
1.3	33
1.5	38
3	76
4	102
5	127
6	152
7	178
8	203
9-3/4	248

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SUMMARY

This report covers the results of investigations directed towards the development of polyimides and polyaromatic melamine (NCNS) resins for the fabrication of high performance composites for structural applications.

In Part I of this investigation polyimide precursors terminated with 5-norbornene groups were processed at 550°F. The curing reaction involved the retro Diels Alder reaction followed by the addition polymerization currently in use with PMR-15 and LARC-160M polyimides.

In order to avoid resin and prepreg instability associated with amic acid precursors stored under refrigeration, novel soluble imide prepolymers end-capped with Nadimide groups were prepared. Solubility in the imidized state was obtained by reacting certain "solubilizing" diamines, i.e., 4-chloro-m-phenylenediamine, 2,4-diaminotoluene, 5(6)-amino-1(4'-amino-phenyl), 1,3,3-trimethylindane and 3,3'-methylene dianiline with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and Nadic anhydride (NA). The imide prepolymers were soluble in THF, dioxane, chloroform, ethylene dichloride or DMF depending on composition. Laminating varnishes and prepregs with good room temperature storage stability were prepared. Vacuum bag-autoclave 550°F processing studies on these resins were carried out but under optimal conditions it was not possible to reduce laminate void contents below 4%. Oxidative aging at 500°F for 1000 hours yielded only 53% retention of initial 500°F interlaminar shear strength. Retention of solvent residues and/or minimal resin flow of these polyimides was believed to be the cause of void formation and poor retention of elevated temperature properties.

The utility of a low cost amine mixture consisting mainly of 2,4-bis(p-aminobenzyl)aniline (BABA) was evaluated for producing imide prepolymers of branched structure and improved processability. Since these imide prepolymers prepared from NA, BABA and BTDA had marginal solubility characteristics solutions of the monomers, i.e., monoethyl ester of NA (NE), BABA and diethyl ester of BTDA (BTDE) were used to develop a 1.85 NE/1.23 BABA/1.00 BTDE resin formulation. Celion 6000 prepreg tapes with this resin had drape and tack for 48 hours at room temperature and were 550°F vacuum bag-autoclave processed to yield laminates of negligible void content and high strength at 600°F. Oxidative aging tests at 600°F for 500 hours showed that 85% of initial 600°F interlaminar shear strength was retained. A procedure for preparing large quantities of this resin for development was demonstrated.

Enhanced resin performance was achieved by replacement of a portion of the NE monomer with monoethyl phthalate. This resin modification, compared to the PMR-15 and LARC-160 polyimides, gave superior prepreg tack and drape, lower resin cost and equivalent laminate processability and oxidative stability.

In Part II of the investigation two novel addition polymerization mechanisms were evaluated for producing 400°F autoclavable polyimides that could be post cured to yield high strength laminates at 500°F or above. The A-2 alternate addition polymerization reaction involved the Diels Alder addition between cinnamal and maleimide groups. Cinnamal end-capped soluble imide prepolymers were prepared from cinnamaldehyde, 4-chloro-m-phenylenediamine and BTDA and cured with bis-(4-maleinimidophenyl)methane. Laminating varnishes that were stable at room temperature were prepared in ethylene dichloride/dioxane mixture or THF. Autoclave processing at 400°F in nylon vacuum bags was carried out to yield laminates of negligible void content. Post cures carried out at 575°F gave laminates with excellent initial strength at 550°F, water resistance and low smoke evolution under flaming conditions. Oxidative aging tests carried out at 500°F showed however that only 50% of the initial 500°F flexural strength of these laminates was retained after 1000 hours. The processing and performance advantages of the A-2 alternate polyimides were consequently nullified by poor oxidative aging characteristics.

The second 400°F addition polymerization reaction investigated involved the Michaels addition of terminal aromatic amino groups of soluble imide prepolymers to the maleimide groups of bis-(4-maleinimidophenyl)methane. Vacuum bag-autoclave processing at 400°F was carried out on prepregs prepared from dioxane based laminating varnishes. The resulting laminates had void contents of 5% or greater and in general were inferior in strength properties and oxidative stability to the A-2 alternate polyimides.

Part III of this investigation involved development efforts on laminates prepared from the N-cyanosulfonamide (NCNS) resins which cured by a novel addition polymerization reaction to yield polyaromatic melamines. This reaction was thermally initiated at 250°F and did not require a catalyst. The NCNS-12M resin prepared from 4,4'-methylenedianiline, benzenesulfonyl chloride and cyanogen chloride was non-burning and left a char content of $\sim$ 60% at 900°C. The solid resin was dissolved in alcohol/ester or alcohol/chlorinated solvent mixtures with heating and prepregs were prepared by the wet winding process. Void free laminates were fabricated by vacuum bag-autoclaving or rapid 3 minute press laminating processes at 350°F. Post cures at 450°F were used to optimize high temperature properties and humidity resistance. The NCNS-12M laminates maintained high interlaminar shear strengths upon 400°F oxidative aging for at least 1500 hours, passed FAA Vertical burn tests and gave low smoke and toxic gas emissions under flaming conditions. The graphite fiber laminates showed no change in 160°F interlaminar shear strength after 67 days at 98% relative humidity with -50°C/+50°C cycling. Retention of 350°F interlaminar shear strength after 30 day, 95% relative, 120°F exposures was 50% which increased to 68% with an additional post cure.

Further improvements were sought in humidity resistance, prepreg tack and drape, and solubility of laminating varnishes. A new resin formulation, NCNS-13P with these improvements was developed. This resin based on the N-cyanosulfonamide of 2,4-bis(p-aminobenzyl)aniline dissolved at room temperature in a variety of solvents and gave prepregs of improved quality. NCNS-13P resin required less than half the post cure time of the NCNS-12M resin to give a thermoset of higher glass transition temperature, lower rate of thermal expansion, and improved 350°F humidity resistance.

A comparative study was carried out on the 350°F humidity resistance of NCNS-13P, Narmco 5208, and Hexcel F-178 graphite fiber laminates. After 30 day, 95% relative humidity, 120°F exposures the NCNS-13P laminate had a 350°F interlaminar shear strength 43% higher than the Narmco 5208 laminate and 60% higher than the Hexcel F-178 laminate.

A pilot plant batch of NCNS-13P resin was prepared for further development efforts. A variety of vacuum bag-autoclave processing procedures were established for preparing void free laminates. Oxidative aging tests at 450°F on a NCNS-13P/AS graphite fiber laminate showed complete retention of 400°F strength properties after 3000 hours. The high char, non-burning, low smoke generating characteristics of NCNS-13P laminates were found to be comparable to those of the NCNS-12M and polyimide laminates.

NCNS-13P resin was found to be a compatible hardener for a variety of epoxy resins and to up-grade their non-burning characteristics and humidity resistance. The NCNS-epoxy blends compared to the NCNS resins melted at a lower temperature and gave quality prepregs in the absence of solvents. These blends were processable at 250°F and gave laminates of low void contents. After post cures at 400°F the laminates had high interlaminar shear strengths at 350°F which showed no decline after oxidative aging at 350°F for 2500 hours. Initial evaluations indicated that NCNS-13P-cycloaliphatic epoxy resin blends had the best storage stability, humidity resistance and lowest smoke generating characteristics.

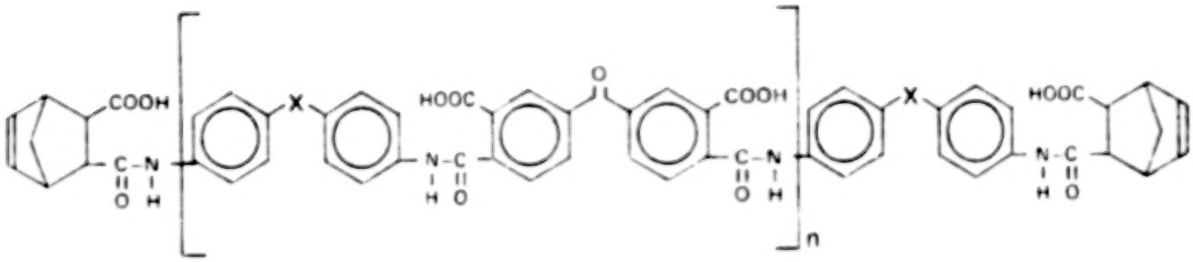
Selected temperature, pressure and linear dimension values in the text are given in U. S. Customary units (°F, psi, inches). A conversion chart is supplied after the Table of Contents.

PART I. ADDITION POLYMERIZED POLYIMIDES WITH 550°F AUTOCLAVE PROCESSABILITY

1. INTRODUCTION

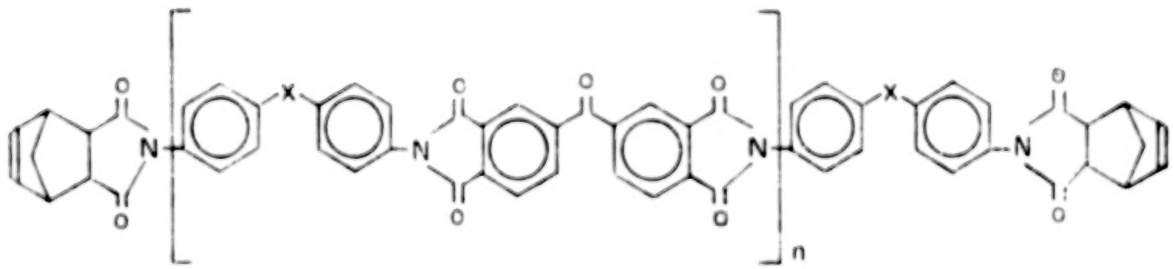
CIBA-GEIGY Corporation manufactured and sold commercially a 550°F autoclave processable polyimide, i.e., P105A, until 4,4'-thiodianiline one of its raw materials, was withdrawn from the market because of possible health hazards. (1) U.S. Government facilities and aerospace companies that had carried out extensive development work with P105A expressed an interest in a replacement which would replicate its processability and performance.

P105A consisted of the following amic acid prepolymer at 35% concentration in DMF solvent.



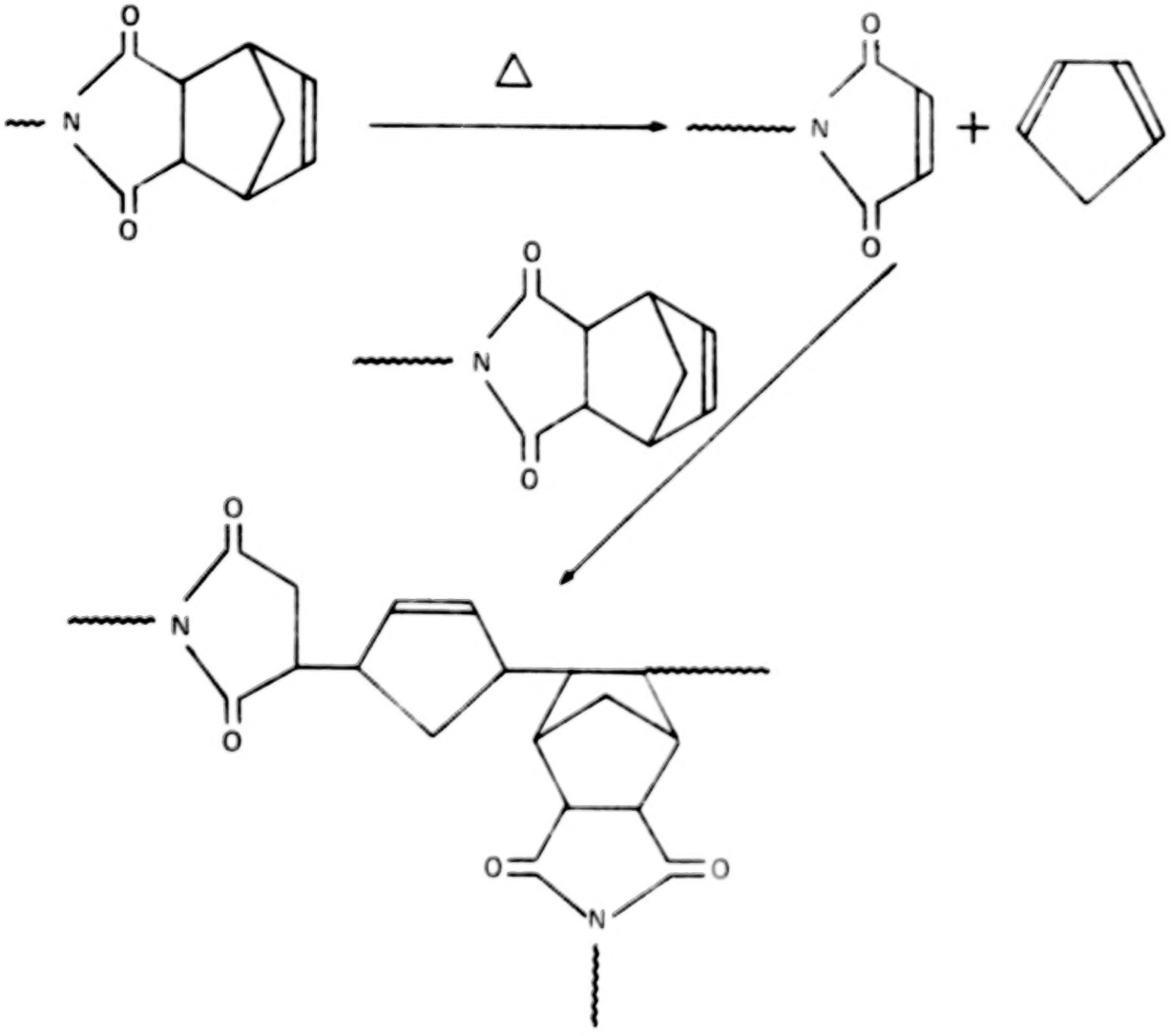
- where X was 80% - $C(H_2)$ - and 20% - S - groups and n = 1.6

The laminating varnish and prepregs required continuous refrigeration before processing. During vacuum bag-autoclave processing the following insoluble imide prepolymer intermediate was formed at 190°C.



The function of the 4,4'-thiodianiline in this imide prepolymer was to depress the melting point to 215°C. At this temperature the melt was stable for a sufficient period to allow residues of DMF and other void causing volatile compounds to be removed before thermosetting of the resin.

Upon raising the temperature above 215°C the terminal Nadimide groups underwent a retro Diels Alder reaction to generate cyclopentadiene and maleimide terminal groups which in turn reacted with residual Nadic imide groups by an addition polymerization mechanism.



This reaction was completed in the autoclave at 550°F and the laminates were then given an unrestrained oven post cure at 575°F for a two hour period.

Serafini, Delvigs and Lightsey[2] made a significant contribution to the technology by developing PMR 15 utilizing the addition polymerization of Nadimide groups while eliminating the use of 4,4'-thiodianiline and DMF. They reacted Nadic anhydride (NA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride

(BTDA) with excess alcohol to yield the monomethyl ester of 5-norbornene, 2,3 dicarboxylic acid (NE) and dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE).

4,4'-Methylene dianiline was dissolved in the alcoholic ester mixture to yield a monomeric solution for prepreg formation. Laminates with improved oxidative stability were produced by 550°F vacuum bag-autoclave processing. The prepregs however were deficient in drape and tack due to volatility of solvents and crystallization of 4,4'-methylene dianiline. Curved parts had to be shaped over heated mandrels for fabrication.

PMR technology was improved by St. Clair and Jewell[3] by preparing the ethyl esters of the above anhydride and replacing 4,4'-methylene dianiline with Jeffamine AP-22, a mixture of 15% polymethylene polyphenylamines and 85% 4,4'-methylene dianiline. This LARC-160M monomeric mixture in the solvent free state could be melt prepregged to yield prepregs with initial 24 hour tack and drape. The 550°F vacuum bag-autoclave processing and resulting laminate properties were similar to those observed with PMR-15.

Identification of commercial products in this report is to adequately describe the materials and does not constitute official endorsement, expressed or implied, of such products or manufacturers by the National Aeronautics and Space Administration.

2. EXPERIMENTAL*

2.1 Preliminary Evaluation

In our initial research effort experimental glass fabric laminates were made with P105A, PMR-15 and LARC-160M resins and oxidatively aged to provide a performance base for evaluating our progress in developing an improved 550°F vacuum bag-autoclavable polyimide resin.

2.1.1 P105A Polyimide

A P105A laminating varnish I-22K-25 was synthesized in the laboratory by the standard production technique of CIBA-GEIGY Corporation. This freshly prepared varnish was given a Torsional Braid curing study. The glass transition temperature was 260°C after a 280°C cure and 392°C after a two hour cure at 300°C. These results were in agreement with published data.[4]

A 181E glass laminate I-22F-28 was prepared from this resin by the standard P105A vacuum bag-autoclave processing conditions shown in Table 1. The physical properties of this 181E glass laminate compared favorably with those of the A-2 alternate polyimides and 550°F autoclavable polyimides. Precut short beam shear samples were oxidatively aged in a forced draft air oven at 500°F for 1000 hours and the retention of initial 500°F short beam shear strength was plotted in Figure 1. After 1000 hours aging approximately 32% of the original 500°F short beam shear strength was retained.

---

*Measurements in this report are expressed in the International System of Units (SI) with the exception of temperatures.

2.1.2 LARC-160M

BTDA, 0.335 moles and 0.610 moles of NA were refluxed in 300 g of absolute ethanol until solution occurred. The mixture was cooled to room temperature and 0.539 moles of Jeffamine AP-22 was added to the solution and stirred until a homogeneous solution was obtained. This solution was used to impregnate 181E glass cloth.

In run no. I-22F-128 the prepreg was heated at 120°C for one hour and excellent processability and laminate properties were obtained as shown in Table 1. In this run resin melt flow was 4% and the resulting laminate contained 29.1% resin and 0.4% void content. The Thermal Mechanical analysis on this laminate showed rapid expansion of the Z-axis commencing at 406°C and actual penetration of the penetrometer at 475°C (penetration mode at 5°C/minute and 100 g load). This data indicated that good mechanical stability was maintained in the critical 300 to 400°C temperature range.

Precut flexural bars of this laminate were oxidatively aged in 500°F in a forced draft air oven for 1000 hours. The retention of original 500°F flexural strength was plotted vs. hours of aging in Figure 2. Retention of elevated temperature flexural strength for the 1000 hour aging period was 75%.

2.1.3 PMR-15

A 7781 glass fabric prepreg batch no. CPI-2237/7781, based on PMR-15 was purchased from Ferro Composites Division. The prepreg was drapable and had sufficient initial tack, due to the presence of solvent, to give a well consolidated lay-up in the vacuum bag.

In run no. I-24A-47, Table 1 fourteen plies 7" x 8" were vacuum bag-autoclaved at 550°F to yield a low void laminate of high strength suitable for oxidative aging studies. Precut short beam shear samples were aged in a forced draft air oven for up to 1000 hours at 500°F. Figure 2 compares the retention of 500°F interlaminar shear strength upon aging the LARC-160M laminate I-22F-128 and the PMR-15 laminate I-24A-47. It was concluded that PMR-15 had slightly better oxidative stability than LARC-160M and the P105A polyimide by far had the poorest oxidative stability.

With respect to prepreg storage stability and oxidative stability of laminates the reactive monomeric solution route was demonstratively superior to the amic acid prepolymer route used with P105A. For this reason the amic acid prepolymer route was not considered worthy of further research efforts. Two approaches remained to be exploited namely, the preparation of hydrolytically stable Nadimide terminated soluble imide prepolymers and the further development of superior monomeric solutions beyond the level of performance achieved with PMR-15 and LARC-160M.

2.2 Soluble Imide Prepolymers

2.2.1 Prepolymers Prepared from 4-Chloro-m-phenylenediamine (CPDA)

Initial success in preparing soluble imide prepolymers with CPDA in the A-2 alternate resin[5] prompted an investigation into preparing 550°F autoclavable resins from a 2 NA/3 CPDA/2 BTDA composition.

Previous experience with preparing soluble imide prepolymers in DMF had shown that DMF formed a solvent complex with the prepolymer. It was impossible to remove the last traces of DMF from the polymer during vacuum bag-autoclaving and the resulting laminates had approximately 10% void content. VPC and elemental analyses indicated that approximately 0.33% by weight of DMF was retained by the polymer.

Efforts were made to synthesize the imide prepolymer without the use of DMF at any step of the synthesis. The amic acid prepolymer was prepared in tetrahydrofuran solvent at 0°C in a 48 hour reaction period. It was then precipitated into water, filtered off and imidized in a vacuum oven at 190°C for one hour. The imide prepolymer yield was 99.1%.

Found	C	63.58%;	H	3.18%;	N	6.56%;	Cl 8.35%
Theory	C	65.05%;	H	2.89%;	N	6.50%;	Cl 8.23%

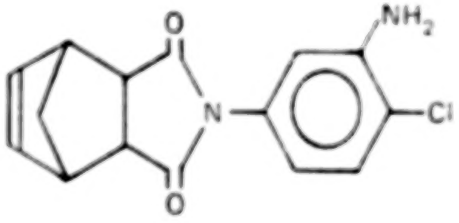
Although the amic acid was soluble in THF when it was later converted to the corresponding imide prepolymer it was insoluble in this solvent. This imide prepolymer was found to be soluble in dioxane however and all of the subsequent processing studies were carried from this solvent.

A Torsional Braid curing study was carried out on a dioxane solution of this prepolymer. After one hour of heating at 550°F the modulus reached a maximum level. At this curing temperature the Tg was 303°C upon heating and 335°C upon cooling. At a post cure temperature of 575°F the Tg was 315°C upon heating and again 335°C upon cooling. Two hours of heating at 575°F were required for modulus to reach its maximum level.

In run no. I-22F-98 the imide prepolymer was dissolved in dioxane at 25% by weight concentration. This laminating varnish was used to prepare 181E glass cloth prepreg which was vacuum bag-autoclave processed as shown in Table 2. The resulting laminate of 4% void content was cut up into flexural bars which were oxidatively aged in a forced draft air oven at 500°F with a P105A/181E glass cloth laminate. The retention of 500°F flexural strength over a 1000 hour oxidative aging period was plotted in Figure 3. This plot shows that for the first 250 hours of aging the P105A laminate had the best retention of elevated temperature properties but at 450 hours the I-22F-98 laminate was comparable in strength retention to the P105A laminate. Strength retention upon aging for laminate I-22F-98 was superior to that obtained for the P105A laminate between 500 and 1000 hours. After 1000 hours of oxidative aging the retention of initial 500°F flexural strength was approximately 53% for the 2 NA/3 CPDA/2 BTDA polyimide.

In run no. I-22F-104 Table 2 the size of the glass cloth laminate was scaled up to 7" x 8" and the vacuum bag-autoclave processing was carried out by the same conditions used previously. This laminate had approximately the same physical properties as the smaller laminate I-22F-98. In run no. I-22F-113, Table 2 a 7" x 8" x 1/8" unidirectional HT-S graphite fiber laminate was prepared by a press laminating procedure in order to maximize strength properties. The properties of this laminate were slightly better than those of the smaller 4" x 5" x 1/8" graphite fiber laminate prepared by the vacuum bag-autoclave process used in run no. I-22F-117. It was concluded that the 2 NA/3 CPDA/2 BTDA soluble imide prepolymer did not yield laminates with outstanding strength properties because the resin flow achieved during processing was never greater than 2 to 3 percent and the laminates consistently retained 4 to 10% void content.

In run I-22F-110, Table 2 a higher molecular weight imide prepolymer of 2 NA/4 CPDA/3 BTDA composition was shown to have even poorer processability. In order to improve the resin melt flow during processing and hopefully reduce the void content of the soluble imide prepolymers based on CPDA a shorter chain version, i.e., 2 NA/2 CPDA/1 BTDA was synthesized. An alternate synthetic procedure was also developed to prepare the following imidized terminal capping group.



NA and CPDA were reacted in refluxing toluene. Within 90 minutes the stoichiometric quantity of water of imidization was collected in a Dean-Stark trap. Upon cooling the toluene to room temperature a first crop, 202 g (70% yield) of the above compound, m.p. 169-183°C was isolated.

Found	C 62.52%;	H 4.42%;	N 9.59%;	Cl 11.70%
Theory	C 62.40%;	H 4.54%;	N 9.71%;	Cl 12.28%

Two moles of the imidized terminal capping group were reacted with one mole of BTDA. The resulting amic acid was imidized for one hour at 190°C. This imide prepolymer melted at 190-200°C which was a lower melting point than the other prepolymers and indicated improved processing characteristics. In run no. I-22F-130 (Table 2) the 2 NA/2 CPDA/1 BTDA imide prepolymer was vacuum bag-autoclave processed by applying the pressure at 420°F. This 181E glass cloth laminate had the best strength properties of any of the CPDA based polyimides but unfortunately still had a void content of 5.1%.

Another attempt to decrease the melting point and increase the resin melt flow during processing was to incorporate a small amount of 3,3'-methylene dianiline into the polymer backbone. An imide prepolymer was synthesized from a molar ratio of 2 NA/2.5 CPDA/0.5 m,m' MDA/2 BTDA. After solution imidization in DMF the imide prepolymer was isolated and found to melt at 205°C and gel within 10 minutes at 215°C. It was soluble in dioxane, ethylene dichloride and their mixtures. In run I-19N-147, Table 2 it was vacuum bag-autoclave processed out of dioxane solvent. No improvement in laminate void content or strength was observed by use of this polymer composition although 20% resin flow was observed during processing. It was hypothesized that CPDA based imide prepolymers terminated with Nadimide groups formed solvent complexes with DMF and dioxane which were not broken by acceptable polyimide processing conditions. These solvent complexes were believed to be the cause of the void formation in these composites. For these reasons a number of other diamines were investigated for preparing soluble imide prepolymers with improved properties.

2.2.2 Prepolymers Prepared from 2,4-Diaminotoluene (DAT)

An amic acid prepolymer of 2 NA/3 DAT/2 BTDA composition was prepared in DMF solution at 0-2°C. Imidization was carried out in refluxing DMF and the imide prepolymer was isolated by precipitation into water. This prepolymer melted at 240-245°C and at 265°C had a gelation time in excess of 15 minutes. The prepolymer was soluble at +30% solids concentration in DMF, THF, and chloroform solvents.

A 181E glass cloth prepreg was prepared from a dioxane solution of this imide prepolymer and vacuum bag-autoclave run no. I-22F-79, Table 2 was carried out. During this run 10% resin flow was observed. The laminate contained 18% void content and its 500°F strength was lower than the other laminates fabricated from imide prepolymers containing CPDA.

2.2.3 Prepolymers Prepared from 5(6)-Amino-1(4'-aminophenyl) 1,3,3-trimethylindane (DAPI)

The isomeric mixture of (DAPI)[6] was reacted with NA and BTDA in a THF-dioxane solvent mixture at 0-5°C to yield a 2 NA/3 DAPI/2 BTDA amic acid prepolymer. The amic acid was isolated by precipitation into water and imidization was carried out in an air oven at 190°C for one hour and 20 minutes. The elemental analysis was as follows:

Found	C 74.09%;	H 5.83%;	N 5.08%
Theory	C 76.52%;	H 4.97%;	N 5.05%

The imide prepolymer melted at 235°C and had a gelation time in excess of 15 minutes at 235°C. After a TBA cure at 316°C the Tg of this polymer was found to be 340°C.

In run no. I-22F-106, Table 2 a 30% resin solids solution in THF was used to prepare a 181E glass prepreg and vacuum bag-autoclave process a 12 ply lay-up. The resulting laminate had 6% voids and 500°F mechanical properties comparable to 181E glass laminates made from the 2 NA/3 CPDA/ 2 BTDA resin composition.

2.2.4 Prepolymers Prepared from 3,3'-Methylene Dianiline (3,3'MDA)

3,3'MDA was reacted with BTDA in a 3/2 molar ratio in DMF for three hours and then NA was added and the reaction was stirred for 17 hours at room temperature. The Nadic capped amic acid prepolymer in DMF was added to distilling DMF. The water of imidization removed during distillation was 98% of theoretical. The soluble imide prepolymer was isolated by adding the DMF solution to a ten fold quantity of water under agitation. The dried resin was isolated in theoretical yield. The resin melted at approximately 165°C, had a gelation time of 60 minutes at 225°C and a Mn by VPO of 1080. This resin was soluble at +30% concentration in p-dioxane and ethylene dichloride and the solutions were stable after two weeks storage. A laminating varnish of 30% resin concentration in dioxane was prepared for processability studies.

A standard P105A 550°F autoclaving cycle was carried out on 181E glass prepregs of this resin; however, the resin melt flow was 47% and only 22% resin was retained in the laminate. In order to avoid excessive resin flow, 181E glass prepregs were B-staged at 225°C for periods up to 1.5 hours; however, high melt flow was observed upon press laminating at 550°F. B-staging at 240°C for 1/2 hour produced moderate melt flow but press laminating at 550°F gave a laminate with poor cohesion between the plies.

2.2.5 Oxidative Stability Tests on 2 NA/3 CPDA/2 BTDA and 2 NA/3 DAPI/ 2 BTDA Polyimide - 181E Glass Cloth Laminates

Thermogravimetric analyses in a nitrogen atmosphere were carried out on the best glass cloth laminates and the results were tabulated in Table 3. The DAPI based laminate I-22F-106 showed the greatest weight loss at 500°C in nitrogen while the CPDA based laminates I-22F-104 and I-22F-87 lost approximately half the weight lost by I-22F-106. The 2 NA/3 DAPI/ 2 BTDA polyimide laminate was cut into short beam shear samples which were oxidatively aged for up to 1000 hours at 500°F in a forced draft air oven. Figure 4 shows that the 500°F interlaminar shear strength decreased linearly over this period.

2.2.6 Insitu Synthesis of Soluble Imide Prepolymers from Monomeric Solutions

Processing of a variety of soluble imide prepolymers by different vacuum bag-autoclave procedures in Table 2 failed to reduce the void content of the composites below 5 to 6%. The question remained if the void problem could be eliminated if these same compositions were prepared insitu during vacuum bag-autoclave processing rather than before prepreg formation. The monomeric approach used with PMR-15 and LARC-160M was thought to be a viable approach for providing this answer.

Methanol solutions of NE, BTDE and the diamines were prepared as laminating varnishes for impregnating 181E glass cloth fabric. The prepregs were then B-staged in an oven at 120°C for 30 minutes to reduce excessive melt flow during processing. These B-staged prepregs were "boardy" and did not possess drape or tack.

In run no. I-22F-30, Table 2 a 2 NE/3 DAT/2 BTDE monomeric mixture on 12 plies of 7" x 8" cloth was 550°F vacuum bag-autoclave processed by the standard procedure used for P105 resin. The resulting laminate had good 500°F mechanical properties but contained 10% voids. Precut flexural bars of this laminate were oxidatively aged at 500°F in a forced draft air oven for 1000 hours. The data from this aging study plotted in Figure 5 showed that after 1000 hours aging the retention of 500°F flexural strength was approximately 65%. This was better retention of high temperature strength properties upon oxidative aging than was obtained by preparing the imide prepolymers before processing. The desired reduction in void content was not achieved; however, the overall results confirmed that the monomeric solution approach resulted in improved oxidative stability.

In run no. I-22F-38, Table 2 a 2 NE/4 CPDA/3 BTDE monomeric mixture on 181E glass cloth was 550°F vacuum bag-autoclave processed. The 500°F interlaminar shear strength of this laminate of 43 MPa was higher than that obtained when the same composition was made and isolated as a soluble imide prepolymer, i.e, run no. I-22F-110, Table 2. Since the void problem with CPDA, DAPI and DAT in these soluble imide prepolymers appeared to be difficult to solve, the direction of the research was diverted to investigating diamines that gave insoluble prepolymers which should have improved solvent release properties.

2.3 Polyimides from Monomeric Solutions of NE, BTDE, and Polymethylene Polyphenylamine Mixtures

PMR-15 compositions prepared from 4,4'-methylene dianiline or other aromatic diamines yield linear imide prepolymers. As the molecular weight of the imide prepolymer was increased above approximately 1500 by reducing the NE concentration the melt flow occurring during processing decreased dramatically so that at 2000 molecular weight it was not possible to obtain composites with optimal properties. For best performance in certain applications it might be desired to have more freedom to vary the ratio of NE, BTDE, and amine reactants than was possible in linear imide prepolymers like PMR-15.

Branched imide prepolymers that have a more spherical rather than linear morphology should have improved melt flow characteristics compared to linear imide prepolymers of the same molecular weight. With the branches terminated with Nadimide groups or other aromatic monoanhydrides polyimides of varying crosslink density and enhanced performance could be prepared.

2.3.1 BABA Mixture

In order to investigate the properties of such branched imide prepolymers a low cost (30¢/lb.) polyamine mixture known as BABA was purchased from DuPont. This mixture was the previously discarded residue from the reaction of aniline and formaldehyde in the manufacture of MDA (see Table 4). It melted at 72-76°C, had a viscosity of 1000 centistokes at 100°C and an elemental analysis close to theory for 2,4-bis(p-aminobenzyl)aniline.

Found	C 78.95%;	H 7.09%;	N 13.69%
Theory	C 79.17%;	H 6.98%;	N 13.85%

Figure 6 shows the Liquid Chromatogram of BABA indicating the presence of a major portion of 2,4-bis(p-aminobenzyl)aniline and lesser quantities of 4,4'-methylene dianiline, 3,3'-methylene dianiline, tetramer, pentamer, (of methylene anilines) and a methyl substituted isomer of 2,4-bis(p-aminobenzyl)aniline. A quantitative analysis shown in Figure 7 was carried out by Gas Chromatographic/mass spectral methods. The major components of the BABA mixture were $\sim$78% 2,4-bis(p-aminobenzyl)aniline, $\sim$15% tetramer, $\sim$ 4% 4,4'-methylene dianiline and $\sim$ 2% isomer of 2,4-bis(p-aminobenzyl)aniline. Repeated GC/MS analyses on several BABA batches showed little or no deviation from this quantitative analysis.

2.3.2 Prepolymers Prepared from BABA

Titration of a number of BABA samples indicated that the amine equivalent in grams was 105 $\pm$ 1. A 3% by weight excess of BTDE and NE esters above the stoichiometric equivalent required to form imide rings was used to prepare a series of monomer mixtures which would yield imide prepolymers upon heating that would be chain terminated with Nadimide groups. Table 5 lists these imide prepolymer compositions along with their melting points. In preparing these compositions the BTDA and NA were heated at reflux for four hours in 10% excess anhydrous ethanol, the BABA was added and the mixture stripped of excess alcohol and heated for one hour in a vacuum oven at 190°C/0.1 mm to yield the imide prepolymers.

The data in Table 5 shows that the Nadimide terminated BABA prepolymer that did not contain BTDA had the lowest melting point at 180°C. The 4.00/2.00/1.00 composition was the lowest molecular weight imide prepolymer containing BTDA and it melted between 195-206°C. Since the addition polymerization normally did not initiate until a temperature of 240-250°C was reached, the 4.00/2.00/1.00 imide prepolymer was potentially more processable than the other compositions of lower Nadimide concentration and higher molecular weight. For this reason it was selected for the first investigation of the processability of the polyimides prepared from BABA.

A Torsional Braid curing study was carried out. Figure 8 shows that at a cure temperature of 210°C the modulus was relatively constant over the one hour heating period. The small increase in modulus that took place in the first twenty minutes of heating could be ascribed to conversion of the monomeric mixture to the imide prepolymer structure. At a cure temperature of 240°C the imide prepolymer structure was formed in fifteen minutes and within the next five minutes melted as shown by the drop in modulus. Between twenty and forty five minutes a small increase in modulus took place. During this period at 240°C a "processing window" apparently existed and upon application of pressure in an autoclave it would be anticipated that imide prepolymer melt flow would take place. After forty five minutes cure at 240°C the modulus increased rapidly signifying that crosslinking of the resin was finally taking place. The Torsional Braid curing study conducted at 275°C and 300°C showed that a constant modulus was achieved in thirty minutes at 300°C but the cure at 275°C required longer than one hour to complete.

2.3.3 Press Laminates of BABA Based Polyimides

An ethyl alcohol solution of the 4/2/1 monomeric composition was used to prepare a 181E glass fabric prepreg. Fourteen plies were heated at 120°C for one hour and 175°C for one hour to remove volatiles and yield the imide prepolymer on the fabric. The plies were laid up and pressed at 350°F/600 psi and the platen temperature was then increased at 5°F/minute until a temperature of 550°F was reached. The laminate was cured for 2 hours at 550°F. Good melt flow occurred during fabrication and 25.5% resin was retained by the laminate. After a four hour post cure at 600°F the laminate was cut into short beam shear samples and the thermal profile of interlaminar shear strength vs. temperature was measured and plotted in Figure 9. Retention of room temperature interlaminar shear was almost complete up to a temperature of 500°F. At 600°F the interlaminar shear strength was approximately 73% of this value.

In Figure 10 the Z-axis thermal expansion was measured on the Thermal Mechanical Analyzer. A very low linear thermal expansion was obtained up to a temperature of 325°C. Above this temperature the thermal expansion increased and the intersection of tangents to the curves below and above 325°C indicated that the glass transition temperature was 342°C.

The high cycloaliphatic content of this 4.00/2.00/1.00 polyimide composition was not expected to yield a polymer with the best oxidative stability. For this reason attention was directed to those compositions with the lowest ratio of Nadimide groups per mole of BTDA. In Table 5 the 1.85/1.23/1.00 composition melted between 235-260°C but the 1.50/1.16/1.00 composition was found to thermoset before melting completely. The 1.85/1.23/1.00 composition was therefore selected for the initial investigation of the oxidative stability of BABA based polyimides.

The 1.85/1.23/1.00 formulation in excess alcohol was used to prepare an AS-graphite fiber unidirectional prepreg by the solvent impregnation technique. Eleven 5" x 5" plies were dried at 120°C and imidized in a vacuum oven at 204°C for 3 hours before press laminating at 550°F/400 psi/1 hour. The laminate had a 500°F short beam shear strength of 75 MPa after a 575°F/2 hour post cure. Precut short beam shear samples were oxidatively aged for up to 2000 hours at 500°F in a forced draft air oven. Figure 11 shows that after 2000 hours the 500°F short beam shear strength was 68 MPa (90% retention of initial strength).

In order to evaluate the 600°F oxidative stability of this resin HT-S graphite fiber was substituted for AS fiber and the resulting laminate of 37% resin content and 57% fiber volume was given a 600°F/2 hour post cure. The initial 600°F short beam shear strength was 39 MPa. The oxidative aging was carried out at 600°F for 200 hours in a forced draft air oven. The plot of the 600°F short beam shear strength at 50 hour aging intervals is shown in Figure 12. In the first 50 hours of aging there was an additional post cure taking place with the results that the 600°F interlaminar shear strength increased to 45 MPa. At the 200 hour interval when the test was terminated the 600°F interlaminar shear strength was 43 MPa. This press laminate met the CAST requirements of 600°F oxidative stability for 200 hours.

2.3.4 Vacuum Bag-Autoclave Processing of BABA Based Polyimides

Preliminary vacuum bag-autoclave trials where a full 28" of vacuum was applied from the beginning of the run caused excessive flow of the monomers into the bleeder cloths leaving a laminate of low resin content. At temperatures above 450°F application of high vacuum might remove cyclopentadiene from the resin as the retro Diels Alder reaction took place. This could prevent a reproducible terpolymerization reaction from taking place between cyclopentadiene, maleimide and residual 5-Norbornene groups. A series of vacuum bag-autoclave runs which applied 2" vacuum at various stages was therefore investigated as shown in Table 6. The main variation in these runs was the temperature at which the 2" of vacuum was applied. In run no. I-25R-43 it was found that excessive melt flow during processing could be greatly reduced if the 2" vacuum was applied only after the lay-up had been first heated in order to produce the amic acid prepolymer.

The laminate resin content, fiber volume, and strength properties were further optimized in run no. I-25R-44, Table 6 where this heating period without vacuum was conducted at 194°F for one hour, imidization was carried out at 400°F for three hours and autoclave pressure was applied at 490°F. This was the first successful demonstration of vacuum bag-autoclave processing of a BABA based addition polyimide where a tacky, drapable prepreg was laid up to produce a void free graphite fiber reinforced laminate with excellent elevated temperature strength. I-25R-44 was cut up into short beam shear samples which were oxidatively aged at 600°F. The initial 600°F short beam shear strength of 37 MPa increased to 46 MPa after 200 hours aging and between 200 and 375 hours declined to 40 MPa.

2.3.5 Optimization Study on BABA Based Polyimides

The good performance of these laminates prepared from BABA based polyimides motivated an optimization study where the effect of graphite fiber quality, monomer purity, resin composition, and vacuum bag-autoclave processing conditions were evaluated.

Due to the variability experienced in the CAST Program with the oxidative stability of HT-S graphite fiber Celion 6000 was recommended by NASA Langley for further development efforts. A series of Celion 6000 graphite fiber laminates of 6" x 6" x 1/8" dimensions were prepared as shown in Table 7.

BTDA from Gulf Development Corporation was purified at the Cranston Pilot Plant by extracting it with acetone to remove tetramethylbenzophenone residues. The BTDA was then heated at 130°C for 24 hours to convert residual carboxylic acid groups to anhydrides. The purified BTDA assayed 0.34 meq/gr of acid and 5.92 meq/gr anhydride which was 95 to 96% of the theoretical assay of 6.21 meq/gr. The NA assayed 98% anhydride and was used without purification as received from Eastman Kodak.

The NE/BTDE mixtures containing the excess ethanol were dissolved in acetone and the BABA (97% of the theoretical to form imides) was added in acetone to the ester solution to give a 35% solids laminating varnish. A wet winding procedure was used where the Celion 6000 tows were pulled through the varnish to give unidirectional graphite prepregs. Prepregs were air dried at room temperature to allow the acetone solvent to evaporate. The drape and tack of these prepregs was evaluated after 24 hours at room temperature and found to decrease as the monomeric mixture decreased in NE content as follows:

NE/BABA/BTDE	
4.0/2.0/1.0	decreasing prepreg drape and tack ▼
3.5/1.83/1.0	
3.0/1.66/1.0	
2.5/1.5/1.0	
2.0/1.33/1.0	
1.85/1.23/1.0	

Vacuum bag-autoclave processing studies on the above compositions disclosed that three different processing procedures could be employed to obtain void free laminates. These procedures shown in Table 8 had the common feature that 2" of vacuum was not applied until the lay-up had been heated at 194°F for one hour. Procedure I, where autoclave pressure was applied at 490°F, worked best when the resin composition had a high NE concentration and the melting point of the resulting imide prepolymer was relatively low. Procedures II and III, which applied autoclave pressure at 525°F and 540°F respectively, appeared to be suitable for processing all of the above resin compositions. Resin flow from these processing procedures never decreased below 30%.

The densities of these laminates were theoretical and within the accuracy of this measurement void content was zero. Initial short beam shear strengths at 600°F increased as the Nadic group concentration increased and the apparent crosslink density increased.

Scanning electron microscope pictures at several magnifications were taken of the cross-sections of each laminate. Two of these are shown in Figure 13 and confirmed the void free nature and uniform distribution of Celion fibers of $\sim$ 7 microns diameter in these laminates.

From each laminate twenty short beam test samples were cut and placed in a forced draft air oven at 600°F for oxidative aging tests. At 100 hour intervals four samples of each laminate were removed from the oven for measurement of 600°F short beam shear strength. Figure 14 plots these strength values for a 500 hour oxidative aging period. After 100 hours at 600°F all of the laminates slowly declined in strength and the extent of the decrease in initial 600°F strength depended directly on the Nadic group concentration in the resin, i.e., 4.0/2.0/1.0 declined the most 1.85/1.23/1.0 the least.

The 600°F oxidative stability of the Celion 6000 unidirectional graphite fiber laminate I-25R-151 (1.85/1.23/1.0 resin) was compared to that of LARC-160M and LARC-160A-3 laminates I-27U-4 and I-27U-5 of Table 1 in Figure 15. After 400 hours of 600°F oxidative aging the Jeffamine AP-22 based LARC resins gradually increased in strength while the BABA based laminate I-25R-151 showed a gradual decline.

The 1.85/1.23/1.0 resin formulation was selected for further development. Figure 16 showed that when the Z-axis thermal expansion was measured on the post cured laminate the Tg was 325°C which confirmed the upper use temperature limitation would be approximately 600°F. Table 9 shows that this resin had an extremely low raw material cost compared to any of the commercially or semi-commercially available polyimide resins described to date. This of course was a reflection of the use of BABA monomer available for $0.30/lb.

Twenty pounds of the resin was prepared in the Kilo Lab for development work (see Table 10). The yield of mixed esters was 99.8% and the acid assay was 214 g/equivalent. This assay remained constant when the mixed esters were stored in the freezer for five weeks. A unidirectional Celion 6000 graphite fiber laminate was made from this resin and the 600°F flexural and interlaminar shear strengths shown in Table 11 were comparable to the published values from PMR-15 and LARC-160 laminates.

2.3.6 BABA Based Polyimide Prepregs

Unidirectional Celion 6000 graphite fiber prepregs were prepared from acetone based laminating varnishes of PMR-15, LARC-160M and two BABA based polyimide resin formulations, i.e., 1.85/1.23/1.00 and 2.5/1.5/1.00. The prepregs were exposed to room temperature conditions until the acetone and alcohol volatile solvents had evaporated (approximately six hours). Tack and drape were then evaluated on these prepregs until all of them were boardy and tack free. The following qualitative differences were observed:

Prepreg	6 Hour Exposure	24 Hour Exposure	48 Hour Exposure	72 Hour Exposure	96 Hour Exposure
PMR-15	boardy no tack	———	———	———	——→
LARC-160	drape and tack	drape and tack	boardy no tack	———	——→
1.85/1.23/1.00	drape and tack	drape and tack	drape and tack	boardy no tack	——→
2.5/1.50/1.00	drape and tack	drape and tack	drape and tack	drape and tack	drape no tack

Prepreg drape and tack retention upon room temperature exposure was directly proportional to the concentration of NE present in the resin.

2.3.7 BABA Based Polyimides Formulated with Monoethyl Phthalate

Although prepreg tack and drape increased with increasing concentration of NE Figure 14 showed that the 600°F oxidative stability of the BABA based polyimides decreased as the concentration of NE in the formulation was increased. A method for increasing prepreg tack and drape while maintaining or increasing laminate oxidative stability was needed. The substitution of a portion of the NE by monoethyl phthalate appear to be a viable approach to this objective. It was anticipated that monoethyl phthalate would give the prepreg the necessary tack and drape and during vacuum bag-autoclave processing chemically react to yield oxidatively stable phthalimide groups. Since BABA was a trifunctional amine as much as one equivalent of monoethyl phthalate per two equivalents of NE could be used to meet the requirements for preparing an imide prepolymer with sufficient Nadimide groups for crosslinking. This approach could not work with PMR 15 based on difunctional 4,4'-methylene dianiline without lowering the crosslinks to the point where elevated temperature strength properties were lost.

Table 12 shows two BABA based polyimide resin formulations where 27% and 17% of the NE was replaced with monoethyl phthalate. Both Celion 6000 graphite fiber prepregs had drape and tack that was retained at room temperature for at least one week. Both prepregs were satisfactorily vacuum bag-autoclaved by Procedure II, Table 8 to yield void free laminates. The initial 600°F short beam shear strengths of these laminates however were decreased between 20 and 30% by the decreased NE content and resulting reduction in initial crosslink density. This decreased strength was more than completely regained after laminate I-27U-10 was oxidatively aged for 100 hours and laminate I-27U-9 was oxidatively aged for 200 hours (see Figure 17). After 500 hours of oxidative aging at 600°F these laminates prepared with monoethyl phthalate had a slightly higher 600°F short beam shear strength than laminate I-25R-151 prepared without monoethyl phthalate.

Table 9 showed that the replacement of NE with monoethyl phthalate had an additional advantage in lowering the raw material cost of the BABA based polyimide resins.

3. CONCLUSIONS - PART I

1. A comparison of three polyimide precursors containing addition polymerizable 5-norbornene groups, i.e. amic acids, soluble imides and monomeric mixtures showed that the latter gave laminates with the lowest void contents, highest strength, and best oxidative stability.

2. BABA[(2,4-bis(p-aminobenzyl)aniline] based monomeric mixtures gave prepregs with lower raw material costs and better handling characteristics than PMR-15 and LARC-160 prepregs.

3. The 600°F./500 hour oxidative stabilities of polyimide/graphite fiber laminates prepared from BABA based, PMR-15 and LARC-160 monomeric mixtures were comparable.

4. Monoethyl phthalate is a practical low cost replacement for a portion of the monoester of 5-norbornene in LARC-160 and BABA based monomeric formulations to achieve enhanced prepreg handling characteristics and laminate oxidative stability.

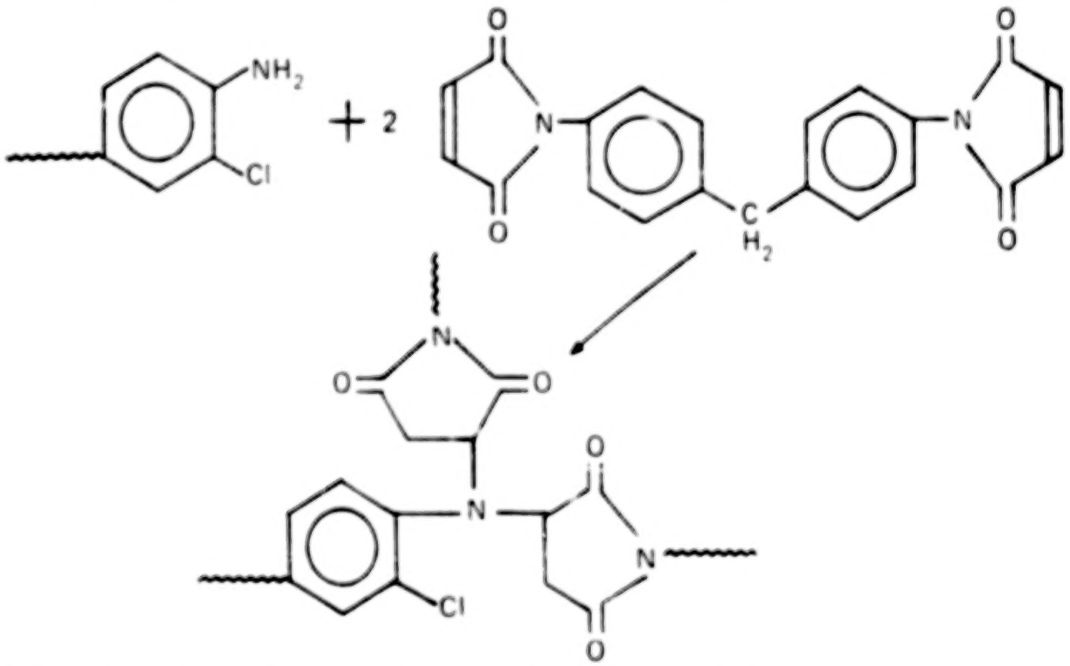
PART II. 400°F AUTOCLAVABLE POLYIMIDES

1. INTRODUCTION

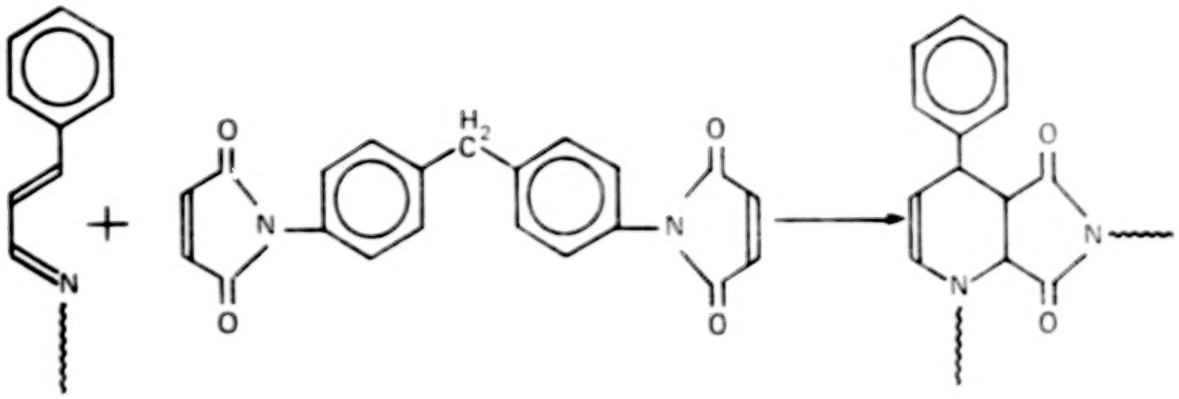
Research had been carried out on the preparation and applications of soluble imide prepolymers that cured by 400°F addition polymerization reactions.[5] Laminating varnishes were prepared at high resin solids concentrations in low boiling solvents and prepregs having drape and tack were vacuum bag-autoclave processed at 400°F to yield low void composites. Postcures carried out on these laminates at 575°F resulted in laminates having good initial mechanical properties at temperatures up to 550°F.

Two of these soluble imide prepolymers offered sufficient promise for further development under NASA Contract NASI-13703. Both had the same imide prepolymer backbone prepared from a 3 to 2 molar ratio of 4,4'-methylene bis o-chloroaniline (MOCA) to BTDA and differed only in their terminal end groups and addition polymerization mechanisms.

A-2 resin cured by the Michaels addition reaction of terminal aromatic amino groups with bis-(4-maleinimidophenyl)-methane(BMI).



A-2 alternate resin cured by a Diels Alder addition reaction between terminal cinnamal groups and BMI.



In 1974 OSHA listed MOCA as a chemical hazardous to health. This furnished the necessary motivation to reformulate A-2 and A-2 alternate resins with a more acceptable commercial aromatic diamine that would like MOCA yield soluble polyimides.

2. EXPERIMENTAL

2.1 A-2 Alternate Polyimide Resins

This resin was given priority over the A-2 resin because of its unique addition polymerization mechanism[7] that suggested superior oxidative stability.

2.1.1 Replacement of MOCA with (CPDA)

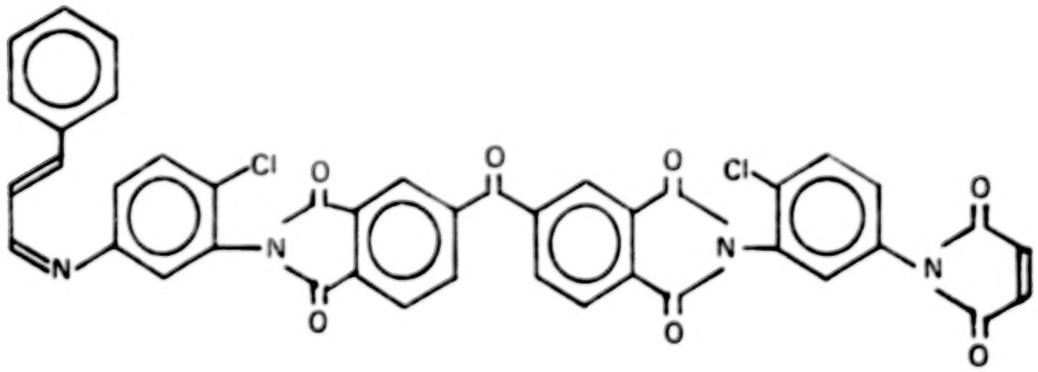
Commercially available CPDA was initially investigated as a replacement for MOCA. Since CPDA has two amino groups of differing reactivity (one sterically hindered by the chloro group) a preliminary investigation was carried out to see if both amino groups would react with BTDA to form a soluble polyimide. An equimolar concentration of CPDA and BTDA was reacted at 0°C for 48 hours at 15% concentration in tetrahydrofuran solvent. Acetic anhydride-pyridine mixture was then added to imidize the polyamic acid. The polyimide was isolated by precipitating it into water. A theoretical yield of polyimide was isolated that was soluble in DMF and had an intrinsic viscosity of 0.83.

Found	C 63.04%;	H 2.26%;	N 6.39%;	Cl 7.72%
Theory	C 64.43%;	H 2.12%;	N 6.53%;	Cl 8.27%

This successful preparation of a high molecular weight soluble polyimide from BTDA and CPDA suggested that CPDA would be an excellent candidate for replacement of MOCA.

2.1.2 One Component Resins

The A-2 alternate polyimide resin contained two components, i.e., a bis cinnamal and bis-maleimide compound that melted together at 150°C and therefore could be processed at relatively low temperatures. The feasibility of having a one component polymer containing both reactive species, i.e., cinnamal and maleimide groups was preliminarily investigated after a successful attempt to make the following compound.



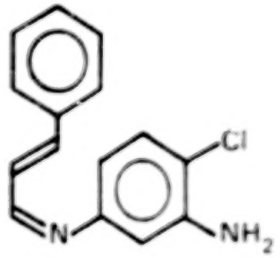
Cinnamaldehyde was reacted with excess CPDA in DMF at room temperature and then the solution was heated at reflux for one hour before distilling off the water of Schiff base formation. Additional DMF was then added and the solution cooled to 0°C before addition of BTDA and maleic anhydride The reaction mixture was stirred for 16 hours at temperatures between 0-8°C. Imidization was carried out at 0°C by addition of an acetic anhydride/triethylamine mixture. The imide prepolymer was precipitated by adding the reaction mixture to a large volume of water. The precipitated product was washed with diethyl ether to remove any unreacted monomer. The dried prepolymer was isolated in 97% yield and melted at approximately 240°C.

Found	C	64.47%;	H	2.89%;	N	7.07%;	Cl 8.64%
Theory	C	65.89%;	H	2.90%;	N	7.32%;	Cl 9.26%

In Torsional Braid curing studies at a cure temperature of 400°F the modulus increased over a two hour period and the Tg was then determined to be 200°C. Upon curing at 550°F the modulus again increased for two hours and the Tg was found to be 320°C. This polymeric system was found to cure at a much slower rate than a two component mixture of bis-cinnamal imide prepolymer with two moles of BMI which melted below 150°C vs. 240°C for the one component system. No further work was carried out with one component resins because of their poorer processability compared to the two component resins.

2.1.3 Synthesis of Cinnamal Terminated Soluble Imide Prepolymers

It was thought that the imide prepolymer could be unequivocally terminated with cinnamal groups if the following compound I could be isolated and then reacted with BTDA and CPDA.

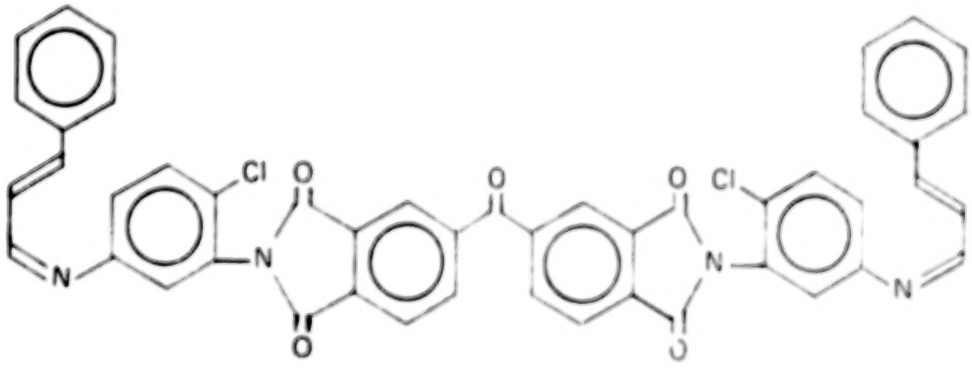


I

An equimolar mixture of CPDA and cinnamaldehyde were reacted as follows. Cinnamaldehyde was slowly added to a toluene solution of CPDA which was being refluxed. The water of Schiff base formation was collected in a Dean Stark trap. A 68% yield of product with a melting point 118.5-120°C was isolated upon cooling the toluene solution to 5°C. The NMR spectrum was consistent with Structure I.

Found	C	69.86%;	H	4.78%;	N	10.83%;	Cl 13.78%
Theory	C	70.18%;	H	5.10%;	N	10.91%;	Cl 13.81%

A 2 to 1 molar ratio of I and BTDA were reacted in DMF at room temperature for 70 hours. The solution was then added dropwise to boiling DMF which was being distilled in order to carry out the imidization in solution. The DMF solution containing the imidized product was isolated by precipitation into water, filtering and drying. The product which melted between 178 to 203°C was believed to have the following structure after infra red and NMR spectral studies.



This prepolymer did not polymerize upon heating at 220°C for 17 hours. The prepolymer was mixed with one mole of BMI and this mixture was found to melt at 127°C and thermoset at 209°C in 5 minutes. A Torsional Braid curing study of this resin was carried out and it was observed that the apparent rigidity of the cured polymer decreased by 29% in raising the temperature from 200°C to 300°C. This was considered an unacceptable decrease in modulus with temperature for high temperature polyimide applications.

Synthetic efforts were then focused on preparing a higher molecular weight cinnamal capped soluble imide prepolymer i.e., 2 cinnamal/3 CPDA/2 BTDA. In order to simplify the preparation I was formed insitu in the presence of excess CPDA and not isolated. A 2/1 molar ratio of CPDA and cinnamaldehyde were reacted together in DMF which was distilled to remove the water of Schiff-base formation from the reaction mixture. A negligible quantity of cinnamaldehyde was present in the distillate. The DMF solution was cooled to 2°C and the BTDA was added to form the cinnamal capped amic acid prepolymer. The amic acid prepolymer solution was then added to DMF which was being distilled. The boiling water generated by imidizing the amic acid prepolymer co-distilled from the reaction mixture with DMF. When the temperature of the distillation vapor increased to 153°C, the boiling point of DMF, imidization was complete. The imide prepolymer was isolated by adding the reaction mixture to a large volume of agitated water. The precipitated prepolymer was filtered off, washed with water to remove occluded DMF and vacuum dried at 160°C to yield the dry prepolymer in +96% yield.

The amic acid prepolymer in DMF was also added to an acetic anhydride/triethylamine mixture at 10°C. Isolation of the imide prepolymer from this chemical imidization process was carried out by precipitation into water, water washing, and drying as above. The following elemental analyses confirmed that the solution imidization process gave soluble imide prepolymers of comparable purity to the chemical imidization technique.

Batch No.	I-24M-3			I-24M-32		
Imidization Process	solution			chemical		
Elemental Analysis						
Found	%C 67.23;	%H 3.63;	%N 7.40;	%C 66.66;	%H 3.13;	%N 6.89
Theory	%C 68.44;	%H 3.04;	%N 6.84			

The solution imidization process was used as the preferred process in the remainder of this work.

2.1.4 2 Cinnamal/3 CPDA/2 BTDA Resins

A 2 cinnamal/3 CPDA/2 BTDA soluble imide prepolymer was prepared having the following analyses and characterization.

- Mn by Vapor Phase Osmometry 1360 (theory 1228)

- Elemental Analysis

Found	C	66.92%;	H	3.17%;	N	7.30%;	Cl	8.38%
Theory	C	68.44%;	H	3.04%;	N	6.84%;	Cl	8.66%

- Melting Point 290°C

One mole of this imide prepolymer and two moles of BMI were blended together to form an A-2 alternate polyimide resin formulation. This resin melted at 165-175°C and at 400°F (204°C) thermoset in 6 minutes. The resin was dissolved at 30% concentration in 50/50 dioxane/ethylene dichloride to prepare a laminating varnish. A Torsional Braid curing study showed that the resin cured to yield a Tg of 365°C. Figure 18 shows that at 400°F the rigidity of the braid increased for about 75 minutes before leveling off.

A 181E glass cloth laminate was prepared by the 400°F vacuum bag-autoclave and post cure process outlined in Table 13. A nylon vacuum bag was found to be ideal for autoclave processing and post curing was carried out without restraint of the laminate in a cam-temperature controlled forced draft air oven.

Table 13 shows that the laminate had no observable voids by density calculations. Cross-sections of the laminate viewed at 30X magnification also appeared void free. The laminate essentially retained its room temperature flexural strength and modulus at 550°F. American Instrument Company smoke density measurements were made under both flaming and non-flaming conditions and the results indicated the A-2 alternate resin had typical polyimide fire resistance and low smoke generation capabilities.

The laminate was cut into four sections which were post cured for 14 hours at 500°F, 550°F, 575°F and 600°F respectively. Short beam shear measurements were made at 500°F and this data was plotted against curing temperature in Figure 19. This plot indicated that a cure temperature in the vicinity of 575°F was optimal. A post cure temperature of 500°F gave an interlaminar shear strength 93% of the maximum value obtained. Post curing at 600°F caused the interlaminar shear strength to decrease to 81% of this maximum value. Thermomechanical analyses measurements on these laminate samples shown in Table 14 indicated that a higher softening point or heat distortion temperature was achieved when the curing temperature was increased.

Two 181 glass cloth laminates I-19N-126 and I-19N-128 of 7" x 9 1/2" x 1/8" dimensions were prepared by the 400°F vacuum bag-autoclave process and post cured at 575°F in order to carry out long term oxidative aging tests. Precut flexural bars were oxidatively aged for 1000 hours in a forced draft air oven at 500°F. The retention of 500°F flexural strength vs. time was plotted in Figure 20. These duplicate laminates after 1000 hours of oxidative aging retained approximately 50% of their initial 500°F flexural strength. This loss in strength occurred to the greatest extent in the first 200 hours of aging and between 200 and 1000 hours 500°F flexural strength was retained.

An effort was made to increase the oxidative stability by decreasing the BMI concentration in the A-2 alternate resin. A Torsional Braid curing study showed that with 1.5 moles of BMI the decrease in modulus in raising the temperature from 200°C to 300°C was 9.7% vs. 8.7% with 2 moles of BMI. Thus little adverse effect on retention of modulus with increasing temperature was noted with this decrease in BMI concentration. With 1.5 moles of BMI per mole of imide prepolymer the resin melted at 190-195°C and had a gelation time of 8 minutes at 204°C. The glass temperatures achieved at various cure temperatures are shown in Table 15. With a 300°C cure temperature a Tg of 310°C was achieved vs. 365°C for the A-2 alternate polyimide cured with two moles of BMI.

The properties of the glass cloth laminate prepared from this resin by the 400°F vacuum bag-autoclave process are given in Table 16. Flexural bars were oxidatively aged at 500°F for 1000 hours and the retention of 500°F flexural strength vs. time was plotted in Figure 20. The oxidative stability was found to decrease as the BMI was decreased from 2.0 moles of BMI to 1.5 moles per mole of imide prepolymer.

Attention was then directed to preparing HT-S graphite laminates for water boil tests to obtain a measure of the environmental water resistance. In run I-19N-150C suitable 400°F autoclave processing conditions for the graphite laminate were found to be as follows:

(1) Heat from room temperature to 275°F in one hour under full vacuum.
(2) Maintain for three hours at 275°F under full vacuum.
(3) Heat to 338°F in 25 minutes and then apply 100 psi pressure.
(4) Heat from 338°F to 400 F in 25 minutes and maintain for two hours at 400°F.

Post cure laminate at 500°F.

The 500°F short beam shear strength before water boil was 35 MPa and after 24 hour water boil 43 MPa. A total of eight samples were measured to confirm this result. This increase in short beam shear strength with water boiling was considered a highly favorable result in this initial screening effort to find a moisture and temperature resistant polyimide.

The 2 cinnamal/3 CPDA/2 BTDA/2 BMI resin formulations was judged to be the most promising of the 400°F autoclavable polyimide candidates. In run no. I-22K-105B a one pound sample was prepared for more extensive evaluation at NASA-Langley Research Center. The imide prepolymer was prepared in 99% yield with the following elemental analysis.

Found	C	67.13%;	H	3.58%;	N	7.62%;	Cl 8.36%
Theory	C	68.44%;	H	3.04%;	N	6.84%;	Cl 8.66%

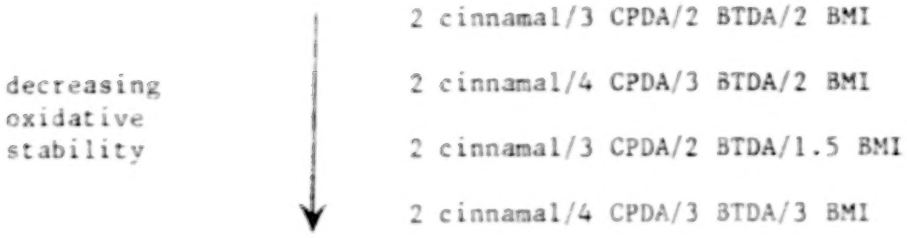
The imide prepolymer and BMI in 1/2 molar concentration were dissolved in dioxane, coprecipitated into water, filtered off and dried. This resin composition had a m.p. of 151-157°C and gel time of 9 minutes at 400°F.

2.1.5 2 Cinnamal/4 CPDA/3 BTDA Resins

In an attempt to improve 500°F oxidative stability of the A-2 alternate polyimide resin a longer imide prepolymer chain was synthesized of composition 2 cinnamal/4 CPDA/3 BTDA. The lower concentration of cinnamal groups on a weight basis could favor improved oxidative stability. This resin dissolved in tetrahydrofuran with BMI at a 1/2 molar ratio respectively to form a room temperature stable laminating varnish at 30% resin solids concentration. A Torsional Braid curing study gave a glass transition temperature of 235°C after a 400°F cure which increased to 325°C after a 572°F cure.

A series of 400°F vacuum bag-autoclave and press laminating trials shown in Table 17 were carried out to produce low void composites with high strength properties for oxidative aging studies. Laminates I-22F-84 and I-22F-96 of 8" x 8" x 1/8" size were cut into flexural test bars which were oxidatively aged in a forced draft air oven at 500°F for up to 1000 hours. A plot of retention of 500°F flexural strength over this period is shown in Figure 21 along with the comparative results achieved with 2 cinnamal/3 CPDA/2 BTDA/2 BMI resin - laminate I-19N-126. This latter laminate retained 52% of its original 500°F flexural strength after oxidative aging for 1000 hours vs only 36% retention of flexural strength for laminate I-22F-84 based on the 2 cinnamal/4 CPDA/3 BTDA/2 BMI resin. Laminate I-22F-96 with a 2 cinnamal/4 CPDA/3 BTDA/3 BMI composition had an even poorer oxidative stability. These results were confirmed by the 500°F oxidative aging results obtain on short beam shear samples of laminate I-22F-90 of identical resin composition (see Table 17).

It was concluded that two moles of BMI per mole of imide prepolymer represented an optimum concentration for best high temperature oxidative stability. The CPDA based A-2 alternate polyimide resins had the following overall order of oxidative stability:


2 cinnamal/3 CPDA/2 BTDA/2 BMI
decreasing oxidative stability
2 cinnamal/4 CPDA/3 BTDA/2 BMI
2 cinnamal/3 CPDA/2 BTDA/1.5 BMI
2 cinnamal/4 CPDA/3 BTDA/3 BMI

2.1.6 2 Cinnamal/3 3,3'MDA/2 BTDA Resins

3,3'-Methylene dianiline was evaluated as a replacement for CPDA in the A-2 alternate polyimide resin. An imide prepolymer containing a 2/3/2 molar ratio of cinnamaldehyde/3,3'MDA/BTDA was synthesized. Imidization was carried out in refluxing DMF. The imide prepolymer had a melting point of 177°C which made it the lowest melting imide prepolymer of A-2 alternate composition. The prepolymer was found to be soluble at 25% concentration in dioxane, chloroform and ethylene dichloride and insoluble in methyl ethyl ketone, ethanol, and glyme.

Intermolecular mixtures of this prepolymer were prepared with m-phenylenedimaleimide, (HVA-2) and BMI (1/2 molar ratios of imide prepolymer to bismaleimide). Both mixtures formed compatible melts in the temperature range between 145-175°C and at a temperature of 204°C (400°F) gelled within 6 to 7 minutes. A Torsional Braid curing study revealed that after a two hour cure at 575°F the glass transition temperature of the polymer was only 265°C. A laminating varnish of the 2 cinnamal/3 3,3'MDA/2 BTDA/2 BMI resin composition was prepared at 30% resin concentration in 50/50 dioxane/ethylene dichloride. A 181E glass prepreg (12 plies - 9.2% volatile content) was vacuum bag-autoclave processed at 400°F by the processing conditions shown in Table 18. During laminating 14% resin melt flow was observed. The laminate appeared void free and contained 34% resin content. Upon post curing at 500°F however severe blistering and delamination occurred presumably because of solvent retention or a glass transition temperature that was too close to the post cure temperature.

No further work was carried out with 3,3'MDA in the A-2 alternate polyimide system because of the low heat distortion temperature of the cured laminates and the lack of commercial availability of 3,3'MDA.

2.1.7 2 Cinnamal/3 DAT/2 BTDA Resins

Commercially available DAT was evaluated in the A-2 alternate polyimide resin formulation. An imide prepolymer with a 2 cinnamal/3 DAT/2 BTDA composition was synthesized and a resin mixture composed of one mole of this imide with two moles of BMI melted at 145°C and gelled within 7 minutes at 204°C. A laminating varnish at 30% resin solids concentration was prepared in 50/50 dioxane/ethylene dichloride solution and 181E glass prepregs were vacuum bag-autoclave processed in run I-22F-27, Table 18 by the processing conditions shown in Table 13. Resin melt flow during processing was negligible and the laminate of 30% resin content contained 8.8% voids.

In summation the A-2 alternate resin with CPDA was more forgiving during processing than with DAT. It showed a better tendency to melt flow at elevated temperatures and gave laminates that were better consolidated, of lower void content, and higher mechanical strength. The DAT containing resin on the other hand appeared to thermoset before solvent release had been completed thereby yielding laminates of high void content.

2.2 A-2 Polyimide Resins

2.2.1 DAT/BTDA Resins

The first effort to replace MOCA in the A-2 polyimide resin involved the evaluation of DAT. In run no. I-19Y-33 DAT and BTDA were reacted in a 3/2 molar ratio in DMF at 10°C. The resulting amic acid prepolymer in DMF was added to boiling DMF over a 4 hour period while DMF and the water formed during imidization was distilled off. To the DMF solution of the imide prepolymer was added BMI in a 1/2 molar ratio of imide prepolymer to BMI. The resulting resin mixture was quantitatively precipitated by adding the DMF solution to a large volume of water. The resin was dried at 60°C/0.1 mm to give a 99% recovery of resin melting at 155-175°C. This resin had a gelation time of 18 minutes at 400°F and was soluble at concentrations of at least 25% in dioxane and DMF.

A second resin was prepared by the procedure described above in run no. I-19Y-138 using a 4/3 molar ratio of DAT to BTDA. This imide prepolymer mixed with two moles of BMI gave a resin that melted at 175-193°C, had a gelation time of 3 minutes - 10 seconds at 400°F, and was soluble in DMF and insoluble in dioxane.

A Torsional Braid curing study was carried out on resins I-19Y-33 and I-19Y-138 and a comparison was made with the A-2 alternate resin 2 cinnamal/3 CPDA/2 BTDA/2 BMI, run no. I-19Y-86A. The data from these curing studies are given in Table 19 and Figure 18. I-19Y-33 cured at both 204°C and 300°C to yield polymers with glass transition temperatures comparable to the A-2 alternate resin. I-19Y-138 after the 300°C cure had a Tg of 330°C some 50°C lower. Figure 18 which plots the increase in modulus with time showed that I-19Y-138 cured at a much slower rate than I-19Y-33 which in turn cured only one half as fast as the A-2 alternate resin. Since the 4 DAT/3 BTDA/2 BMI resin was not soluble in dioxane, was slower curing, had a higher melting point and gave a lower Tg than the 3 DAT/2 BTDA/2 BMI resin the latter was selected as the A-2 polyimide for further development.

A laminate varnish of the resin was made with dioxane solvent for the preparation of 181E glass cloth prepregs. Two vacuum bag-autoclave processing runs shown in Table 20 were carried out under identical conditions on laminates of different size. The initial 500°F mechanical properties were approximately the same and quite comparable to those achieved with the A-2 alternate polyimide resin. This A-2 polyimide resin however gave laminates with higher void contents than the A-2 alternate polyimide resin.

Laminate I-22F-14 was cut into flexural bars which were oxidatively aged for 1000 hours at 500°F in a forced draft air oven. A plot of the retention of initial 500°F flexural strength vs aging time was made in Figure 21. Laminate I-22F-14 retained approximately 38% of its original 500°F flexural strength after 1000 hours at 500°F vs. 50% for the A-2 alternate polyimide laminate. Up until approximately 450 hours of aging both laminates were roughly equivalent in oxidative stability.

2.2.2 CPDA/BTDA Resins

These resins were prepared in order to answer the following question. Was the superior oxidative stability of the A-2 alternate resin compared to the A-2 resin due to the difference in addition polymerization mechanism or due to CPDA being more oxidatively stable than DAT?

Tetrahydrofuran was used as the solvent to form the amic acid from a 4/3 molar ratio of CPDA to BTDA. The amic acid was isolated by precipitation into water and then imidized in an oven for one hour at 190°C. Infra red spectra of KBr discs of the imide showed that all residual amic acid groups had been converted to imide groups after this one hour imidization. The imide prepolymer was very soluble in dioxane and THF.

The imide prepolymer was dissolved in dioxane with two moles of BMI per mole of imide to prepare a laminating varnish of 25% resin solids concentration. Table 21 shows the processing conditions and physical properties obtained upon fabricating 181E glass cloth laminates. The 400°F vacuum bag-autoclave processing cycle used in run I-22F-102 had been previously found to yield void free composites from A-2 polyimides prepared with MOCA diamine. In run I-22F-102 with CPDA however the laminate contained 11% voids and the 500°F short beam shear strength was low. In runs no. I-22F-33, I-22F-36, and I-22F-41 the PMR or monomer approach was used in an attempt to produce a void free laminate from a mixture of CPDA, BMI, and the dimethyl ester of BTDA. The 4 CPDA/3 BTDE/2 BMI monomeric mixture was dissolved in dioxane at 40% solids content to yield a laminating varnish. The monomeric mixture on 181E glass prepregs had negligible melt viscosity and was almost completely removed from the lay-up upon the application of vacuum and pressure during the autoclave cycle. To decrease the flow it was necessary to B-stage the prepreg in an oven at 248°F for 30 minutes. The boardy prepreg was then laid up and vacuum bag-autoclave processed. Resin flow was satisfactory and varied between 3 and 6% and the laminates contained 32-33% resin. In run no. I-22F-36 and I-22F-41 where the vacuum was maintained between one and three hours at 257°F the physical properties were considerably higher than in laminate I-22F-33. All of the laminates however contained at least 9 to 10% void content and were not suitable for oxidative aging tests.

This processing study indicated that BMI reacted with the terminal amino groups of the imide at 302°F causing thermosetting before solvent release was completed. In addition it was concluded that due to the high reactivity of BMI at temperatures below those necessary to complete the imidization process the PMR process did not offer a good approach for obtaining low void composites with A-2 polyimides or A-2 alternate polyimides.

3. CONCLUSIONS - PART II

1. Addition polymerizable soluble imide prepolymers, cured by a Diels Alder reaction, could be vacuum bag-autoclave processed at 400°F. to yield void-free laminates with high strength at elevated temperatures.

2. Addition polymerizable soluble imide prepolymers, cured by a Michaels addition reaction, could be vacuum bag-autoclave processed at 400°F. to yield laminates with high strength but with unacceptable void contents.

3. Both of these 400°F. processable polyimides were deficient in oxidative stability compared to polyimides that had to be processed at 550°F. or higher temperatures.

PART III. NCNS RESINS

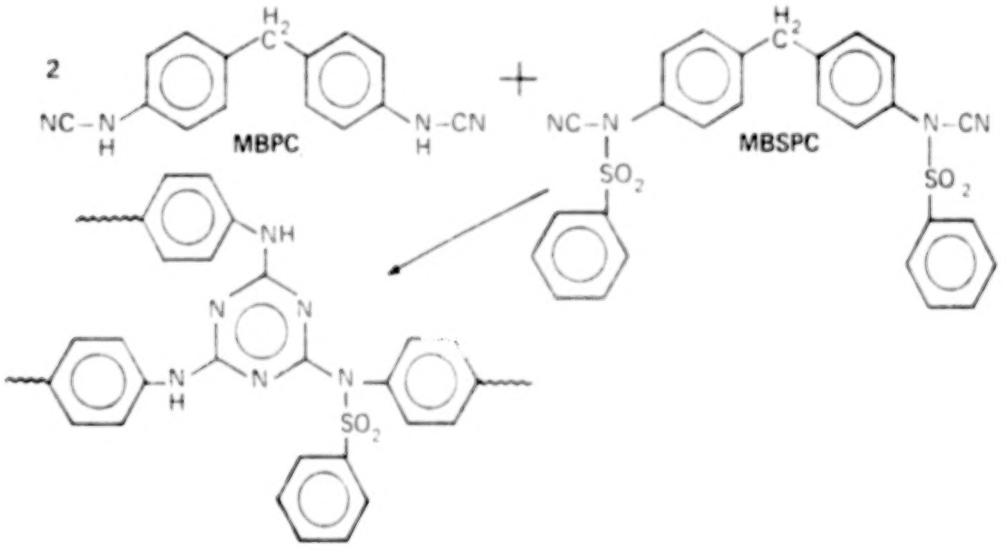
1. INTRODUCTION

The need for a potentially low cost heat resistant thermosetting resin that would combine all of the following performance characteristics had been recognized for a number of years.

- Ease of vacuum bag-autoclave processability into composites with a negligible void content.
- Long term retention of elevated temperature strength after exposure to air at 450°F.
- Retention of strength after exposure to high humidities and temperatures.
- Inherent non-flammability and low evolution of smoke and toxic gases.

Research efforts by CIBA-GEIGY Corporation culminated in the discovery and development of the NCNS resins (N-cyanosulfonamide resins) in 1972 to meet the above performance requirements.[8]

The first NCNS monomers were derived from 4,4'-methylene dianiline reacted with cyanogen chloride and benzenesulfonyl chloride.[9] These monomers, i.e., 4,4'-methylene bisphenylcyanamide (MBPC) and 4,4'-methylene bis (N-benzenesulfonyl phenylcyanamide) (MBSPC) were copolymerized in various ratios to form compatible melts which cured to yield crosslinked aromatic polymelamines. The nitrile groups of each monomer reacted by an addition polymerization mechanism that did not generate volatile compounds.



This reaction was thermally initiated and did not require a catalyst. The NCNS resin in order to replace or supplement the current epoxy resins as composite materials would have to be of low cost, yield storage stable prepregs, be highly processable by a wide variety of techniques, and have good long term retention of high strength at elevated temperatures and humidities.

A number of specific requirements had to be met to successfully develop a processable polymer containing alternating aromatic and melamine groups. First of all it was necessary to develop a meltable precursor that would be highly soluble in readily available, low boiling, non-toxic solvents. This precursor or prepolymer would have to form a stable laminating varnish and yield prepregs having good drape and tack. On the other hand the solvent release properties of the prepolymer had to be satisfactory so that the solvent would be completely removed before gelation of the prepolymer took place upon heating. The prepolymer also had to retain the proper reactivity so that it would polymerize by an addition mechanism that would release no volatile compounds that might form voids in fabricated structures. This curing mechanism also had to impart the necessary rigidity, oxidative stability, non-flammability and water resistance expected of a high performance resin.

2. EXPERIMENTAL

2.1 NCNS-12M Resins

2.1.1 Evaluation of Unidirectional Graphite Fiber Laminates

NCNS-12M resin was prepared from a 1/2 molar ratio of MBSPC to MBPC. The monomers were dissolved in 60/40 methanol/ethyl acetate and heated at reflux for four hours to yield a laminating varnish of 50% resin solids concentration. A undirectional HT-S graphite fiber prepreg was prepared on a drum winder using this varnish. The prepreg was cut into 8 3/4" x 9 3/4" plies and 12 plies were laid up to prepare a 1/8" thick laminate. The press laminating and post curing conditions and laminate characterization data are shown in Table 22.

The laminate was cut into short beam shear test pieces which were placed in a forced draft air oven at 400°F for 1500 hour oxidative aging tests. Samples were removed at 250 hour intervals and the short beam shear strength was measured at room temperature and 400°F. These data are given in Table 23. The room temperature short beam shear strength after some initial increase remained constant for the duration of the test. The 400°F short beam shear strength decreased about 13 percent over the 1500 hour interval.

Short beam shear samples were also boiled in water for 24 hours and their strength was measured at room temperature and 350°F. Table 24 shows no deterioration of room temperature short beam shear strength, rather a 25% increase from water boiling. At 350°F after water boiling an 85% retention of initial strength was achieved. NCNS/HT-S unidirectional graphite fiber laminates in preliminary tests showed no change in room temperature or 160°F short beam shear strength when exposed 67 days to 98% relative humidity in a -50°C/+50°C temperature cycle.

A more severe humidity aging test was employed in the following work. Five short beam shear samples of each graphite fiber laminate were exposed in a Blue M Humidity Chamber for 30 days at 95% R.H., 120°F and the retention of 350°F short beam shear strength over this exposure period evaluated. The exposed samples after removal from the Humidity Chamber were held in a 100% humidity atmosphere at room temperature until tested on the Instron. The wet samples were heated to 350°F within 3 minutes in the Instron chamber and tested immediately before water was lost from the samples. This evaluation procedure is referred to as "humidity aging" in this report.

Table 25 shows the results from three NCNS-12M graphite fiber laminates upon measuring retention of initial 350°F short beam shear strength after humidity aging. These laminates retained approximately 45% of their original 350°F short beam shear strength.

Laminate I-24A-79 was prepared to evaluate the effect of post cure temperature and time on humidity resistance. One half of the laminate was given a 22 hour post cure at 400°F. This half retained a 350°F short beam shear strength of 45 MPa after humidity aging vs. 35 MPa for the two previous laminates initially post cured at 450°F. The second half of the laminate I-24A-79 was given a two step post cure of 400°F/22 hours followed by a 24 post cure at 450°F. This laminate had a 350°F short beam shear strength of 55 MPa after humidity aging which was approximately 80% retention of original strength. The NCNS-12M resin system required at least 48 hours of post cure to obtain maximum resistance to humidity.

2.1.2 Vacuum Bag-Autoclave Processing

The NCNS-12M resin in order to qualify as a candidate resin for aerospace applications had to be vacuum bag-autoclave processable. A study was initiated on this processing method.

A 181E glass prepreg was prepared from the NCNS-12M resin at 50% solids concentration in 60/40 methanol/ethyl acetate solution. The prepreg had good initial tack and drape and was promptly laid up in a nylon vacuum bag and processed. The processing cycle and physical properties of the laminate are shown in Table 26.

During processing the resin flow was 5% and the resulting laminate had excellent appearance. Density measurements indicated that the void content was negligible. The room temperature and 400°F mechanical properties of this laminate on initial evaluation appeared to be approximately 90% of the strength of press laminated samples. Retention of room temperature properties up to 400°F was 76%. It was concluded that the resin could be successfully vacuum bag-autoclave processed at pressures as low as 100 psi with little sacrifice in high temperature strength properties. This vacuum bag-autoclave cycle had to be extended (see Table 26) however in order to completely remove solvent residues when

unidirectional HT-S graphite fiber reinforcement rather than glass cloth was used. The glass cloth due to its weave was relatively "open" compared to the tightly packed unidirectional graphite fibers that presented a barrier to solvent escape. The hold time at 158°F under vacuum was extended from 1 1/2 to 3.0 hours. This process gave a laminate with only 0.2% voids. The 400°F interlaminar shear strength of the laminate was about 90% of that of press laminates. It was only necessary to use a maximum autoclave temperature of 350°F in order to give a high strength laminate for oven post cure 450°F.

2.1.3 Flammability and Smoke Characterization Data

Kevlar 49 fabric and 181E glass fabric laminates were prepared and evaluated for flammability and smoke characteristics. These data given in Table 27 were determined on a Rohm and Haas Smoke Density apparatus. The NCNS laminates had smoke rating densities of 32% and 39% for glass and Kevlar respectively. The specifications of the FAA require in the vertical burn test 25.853A self-extinguishing after flame withdrawal within 15 seconds. The burn length or charred section may be eight inches in length - the NCNS laminates had burn lengths of 1.3 to 1.5 inches. The FAA requirements allow dripping but the drips must self-extinguish in 5 seconds. The NCNS laminates were non-dripping.

In further pursuit of additional flammability and smoke generating data a 181E glass laminate was evaluated using the more accurate American Instrument Company Smoke Density Chamber under both flaming and non-flaming conditions.[10] These data were tabulated in Table 28 where a comparison was made with a P13N polyimide/181E glass laminate. The 181E glass laminate had a maximum specific optical density Dm that was extremely low under both flaming and non-flaming conditions and quite comparable to the P13N polyimide. The time in minutes for a specific optical density $D_s = 16$ to develop was considered by the FAA as the time that a passenger had to reach the aircraft exit since higher smoke densities would obscure the exit signs. Under flaming conditions the laminate required 6.6 minutes to reach this smoke density value - the P13N laminate - 7.5 minutes. Under non-flaming conditions this smoke density was not reached at all by either laminate. The oxygen index data shown in this table indicated that neither the NCNS resin nor P13N would burn in air and an atmosphere of 86% oxygen was required before this NCNS-glass laminate started to burn.

A comparison of the smoke generated under flaming conditions on NCNS glass cloth, NCNS/Kevlar 49 fabric and NCNS/unidirectional HT-S graphite fiber laminates is given in Table 29. Relatively low smoke values were obtained on all of these NCNS laminates but with respect to the reinforcing fibers the lowest smoke values were obtained with glass, then Kevlar, and lastly graphite. Smoke increased in the same order as the decrease in density of reinforcing fiber and the increase in resin content of the laminate.

In order to obtain optimal data new laminates were fabricated having no more than the minimum weight percent resin content required for maximum laminate strength. A NCNS-12M/181E glass cloth laminate of 23% resin content in the Smoke Density test in the flaming mode gave a corrected Dm of 21 and required 8 minutes to achieve a specific optical density of 16 as shown in Figure 22. A NCNS-12M/HT-S graphite fiber laminate of 60% fiber volume and 34% resin content tested in Figure 23 required 3 minutes to develop a specific optical density of 16 and gave a corrected Dm of 52 in the flaming mode. The laminate was examined after the 20 minute test at the spot where the flame impinged. No graphite fibers were exposed and the laminate was only slightly swollen.

In comparative tests conducted on the same instrument, epoxy laminates completely disintegrated and gave Dm values of several hundred within minutes after starting the test.

2.1.4 NCNS-12M Neat Resin Properties

For an evaluation of char contents, fire retardancy, and water absorption a procedure for molding thick sections of unfilled resin was required. The following process was developed to yield 1/2" thick plaques for these tests. The press was heated at 10°F/minute until a temperature of 400°F was reached while maintaining 300 psi pressure. The molded piece was held at 400°F/300 psi for 5 minutes before ejecting from the press while hot. The plaque was post cured by heating it in a forced draft air oven in 5 hours from room temperature to 450°F and maintaining 450°F for 19 hours.

This procedure produced plaques which could be machined and were uniform and homogeneous in cross-section. Thin 1/8" plaques were also successfully made by this procedure that appeared uniform when examined through a high intensity light. The physical properties of plaque I-24A-81 are given in Table 30. Upon heating the molded plaques in an inert atmosphere to 900°C the NCNS-12M resin left 59% char (see Figure 24).

2.1.5 Study on Optimum Post Cure Temperatures

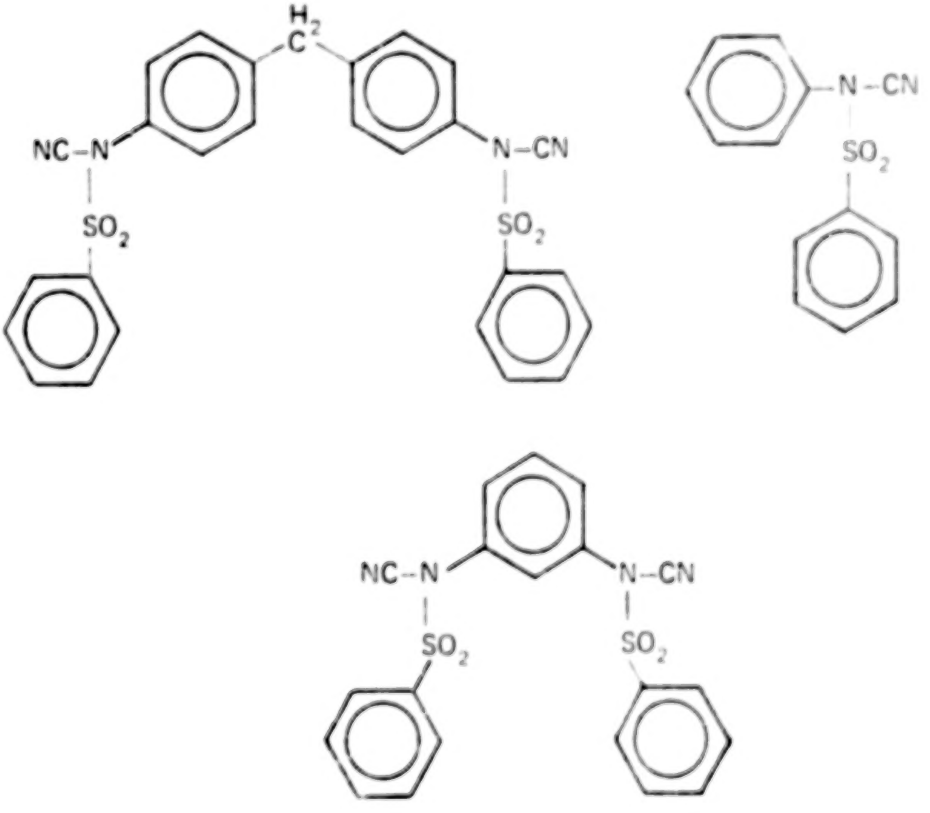
To insure that maximum mechanical strength at elevated temperatures was being obtained with NCNS resins a post cure study was carried out on a NCNS-12M/181E glass laminate. The data in Table 31 shows that although the room temperature properties were not increased by a post cure at 400°F or 425°F the properties at 400°F underwent improvement. Post cure times of 14 hours at 400°F showed marginal increases in 400°F flexural strength, modulus, and short beam shear strength while post cures at 425°F gave greater increases in strength. The Thermomechanical Analyzer penetrometer also showed corresponding increases in the Tg or "heat distortion temperature" particularly with 14 hour cures at 400°F. Post

cures at 400°F, 425°F, 440°F, 450°F, and 460°F were carried out for 14 hours and four short beam shear specimens at each temperature were tested at 400°F. A plot of this data in Figure 25 shows that the highest interlaminar shear strength was achieved with a 440°F post cure temperature. These laminates were also evaluated using the penetrometer attachment on the Thermomechanical Analyzer and this data is shown in Table 32. The heat distortion temperature increased with increased post cure temperature up to a post cure temperature of 450°F.

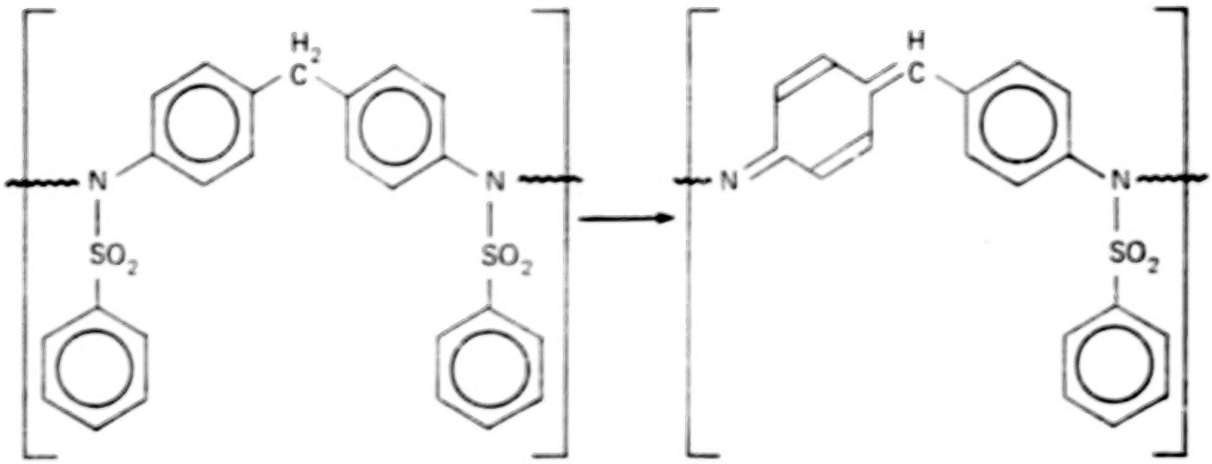
2.1.6 Thermal Degradative Mechanism of the NCNS-12M Resin

In order to optimize the high temperature performance of the NCNS resins a study was made of the degradation products that were produced at elevated temperatures. Samples of a NCNS-12M/HT-S graphite fiber laminate were placed in evacuated break seal tubes which were heated at 220°C for 600 hours. During this period the laminate samples lost 2.6% weight. A white residue was isolated from these tubes whose analyses showed to be a mixture of thiophenol, diphenyl disulfide, and urea type material. The volatile residues were shown to be a mixture of carbon dioxide, water, benzene, hydrogen sulfide and ammonia. The inference was drawn from these results that the degradation mechanism was quite complex and depended on concentration of N-cyanosulfonamide compound.

When the following N-cyanosulfonamide compounds were homopolymerized at 250°C for 24 hours in an evacuated ampoule the generation of thiophenol and diphenyldisulfide was only detected with MBSPC. This observation tended to indicate that the methylene groups significantly contributed to the thermal degradation of the NCNS resin.



A 1-6 elimination reaction was proposed to explain the thermal degradation mechanism of the NCNS resins.



In support of this mechanism it was observed that NCNS laminates oxidatively aged for long periods at 600°F lost sulfur content and weight corresponding to the loss of one mole of sulfonic acid per mole of MBSPC.

The NCNS resins were also evaluated in pyrolysis experiments in an inert atmosphere. An unfilled (neat) compression molding of NCNS-12M resin was post cured at 500°F and this molding was pyrolyzed at 1000°C in a helium atmosphere using a F&M model 80 pyrolysis unit. The pyrolysis products were then analyzed by a Gas Chromotograph-Mass Spectrometer using a 6 foot 2.5 mm i.d. parapak Q glass column programmed from 120°C to 210°C at 10°/minute. The pyrolysis products were scanned continuously with the mass spectrometer as they eluted from the gas chromatograph. Three components were detected in the following order of elution CO_2, SO_2, and benzene.

2.1.7 NCNS Resins with High Ratios of MBPC to MBSPC

An investigation was carried out to evaluate the effect on physical properties of increasing the molar ratio of MBPC to MBSPC in the NCNS resin. A 1:3 MBSPC/MBPC laminating varnish was produced by refluxing the monomer mixture at 50% solids concentration for 70 minutes in 60/40 methanol/ethyl acetate. Despite the short gelation time of this resin it was possible to completely remove the solvent from the prepreg under standard B-staging conditions and obtain good melt flow by press laminating at 435°F. Post cured short beam shear samples of the NCNS-13M/181E glass laminate were oxidatively aged at 400°F for 1000 hours. The plot of 400°F interlaminar shear strength against time in Figure 26 showed that there was essentially no decrease in high temperature strength properties over this period.

In order to evaluate the water and humidity resistance of the NCNS-13M resin a HT-S unidirectional graphite fiber laminate was fabricated. Short beam shear samples were tested at 350°F before and after humidity aging and 54% of the initial interlaminar shear strength was retained after humidity exposure. This was not considered a significant improvement over that obtained with NCNS-12M resin.

2.1.8 Storage Stability Tests on NCNS-12M Resin

A NCNS-12M resin sample was prepared for one year room temperature storage stability tests. The technique for its preparation consisted of dissolving a 1 to 2 molar ratio of MBSPC and MBPC in hot acetone at 50% concentration and then reprecipitating the monomer mixture quantitatively by adding the hot acetone solution to a rapidly stirred tenfold excess of petroleum ether. During the year the container was opened frequently to obtain resin for composite evaluations. After one year the following comparison was obtained:

	Original 9/74 Measurements	9/75 Measurements
Volatile Content (150°C., 15 minutes)	1.25%	1.52%
m.p. °C	123	123
Gelation Time at 140°C	90 seconds	80 seconds

The increase in volatile content could be explained by the absorption of a small amount of moisture during periodic removal of portions of the sample during the year. To see if this increase in moisture content interfered in any way with processability and physical properties a laminating varnish was prepared at 50% solids content in 60/40 methanol/ethyl acetate. A 181E glass prepreg was prepared and dried at 158°F and B-staged at 194°F by the standard procedures developed for the NCNS-12M resin. The laminate containing 15 plies was molded at 350-400°F and post cured at 450°F. Its physical properties at 400°F given in Table 33 were within 80 percent of those obtained from freshly prepared resin at 27% resin content on 181E glass fabric. Shelf stability would be anticipated to have been better if the sample container had remainded sealed during this one year period.

Two drying procedures were found useful for returning this NCNS resin to specification limits. Drying the sample in a forced draft air oven at 50°C for 16 hours brought the volatile content to 0.4%. Drying in a vacuum oven at 45°C/1 mm for the same period brought the volatile content to 0.2%.

Drying temperatures in excess of 50°C were not recommended because of a possible change in the melt pot life or processability of the resin.

The storage stability of a NCNS-12M 60/40 methanol/ethyl acetate laminating varnish was evaluated. An effort was made in run no. I-24A-14, Table 34 to process a 50% resin solids laminating varnish that had been stored for 30 days at room temperature. A 181E glass prepreg was prepared from this aged varnish and B-staged at 302°F for 15 minutes vs. the 230°F/15 minute B-staging given the prepreg in run no. I-24A-3 which was made from a varnish that had been freshly prepared within 24 hours. Both the I-24A-3 and I-24A-14 prepregs were then press laminated and post cured under identical conditions. During press lamination the resin melt flow was identical for both laminates indicating that the more severe B-staging given the prepreg prepared from the 30 day old varnish had successfully prevented the excessive melt flow previously observed with this material. The higher resin content of laminate I-24A-14 was due to the more viscous nature of the 30 day old varnish which resulted in greater resin pick-up on the glass during prepregging operations.

The NCNS resin at 50% resin solids concentration in 60/40 methanol/ethyl acetate solution was also used to prepare 181E glass cloth prepreg for storage stability tests. The properties achieved with the freshly prepared prepreg are given in run no. I-22F-132, Table 35. The prepreg was B-staged at 194°F/15 minutes and converted from a wet, tacky to a dry, boardy state and stored at room temperature for 30 days before press lamination. Run no. I-22F-132A showed that this room temperature storage period for dry prepreg had little adverse effect on the 400°F mechanical properties of the resulting laminate. Similar good retention of 400°F mechanical properties prepared from wet, tacky, non B-staged prepregs that had been stored for 30 and 60 days was achieved in runs no. I-24A-11 and I-24A-25 respectively.

In order to retain solvent for tack and drape properties these prepregs were wrapped in polyethylene film for storage periods up to 90 days. As the prepreg aged it required a higher temperature of B-staging in order to prevent excessive melt flow during lamination. By increasing the B-staging temperature the melt flow was maintained between 1 and 2% and a press laminate containing 30% $\pm$ 1% resin was produced. Figure 27 showed that the temperature of B-staging had to be increased in 5°C increments for every additional 30 day storage period from the first day in order to maintain the resin melt flow below this 2% target level. By this technique, there was no problem in producing a laminate of reproducible resin content, free of voids, and of good elevated temperature mechanical properties from prepreg that had been stored for as long as three months in the tacky, drapable state.

2.1.9 Rapid Processing Cycles for NCNS-12M Resin Prepregs[11]

In order to obtain laminates with excellent elevated temperature properties it was not necessary to compression mold for more than three minutes before giving the laminate an unrestrained oven post cure. The NCNS resins were therefore excellent resins for the fast production cycles required for the economical production of composite parts. Table 36 shows that there was negligible difference in the 400°F flexural strength and interlaminar shear strength of 1581 glass fabric composites whether compression molded for an hour or for 3 or 5 minutes. In addition, it was found that these rapidly molded laminates only required a two hour oven post cure to achieve elevated temperature strengths equivalent to those laminates post cured for 18 hours.

2.2 NCNS Resins Prepared from Polymethylene Polyphenylamines[12]

In order to prepare NCNS resins with the lowest potential raw material cost work was carried out to evaluate NCNS resins made from condensation products of aniline and formaldehyde, i.e., polymethylene polyphenylamines (See Table 4, Figures 6 and 7). These products contained ortho-ortho, ortho-para, and para-para mixtures of methylene aniline with several aromatic rings. The rings were connected by methylene linkages that were stable to water hydrolysis.

2.2.1 NCNS-12J Resins

Jeffamine AP-22 was reacted with cyanogen chloride in a methanol/$NaHCO_3$ water slurry to yield the cyanamide in 99.5% yield.

Found	C 71.76%;	H 4.77%;	N 22.29%
Theory	C 72.97%;	H 4.92%;	N 22.10%

Jeffamine AP-22 was also reacted with benzenesulfonyl chloride in the presence of triethylamine in tetrahydrofuran solvent to give an 85% yield of the crude N-phenylsulfonamide m.p. 65-70°C.

Found	C 61.95%;	H 5.35%;	N 5.74%;	S 12.46%
Theory	C 62.87%;	H 4.64%;	N 5.80%;	S 13.34%

The N-phenylsulfonamide was reacted with cyanogen chloride in THF in the presence of triethylamine to yield the corresponding N-cyanosulfonamide compound, m.p. 45-50°C., yield 84%.

Found	C 61.52%;	H 3.92%;	N 10.74%;	S 11.82%
Theory	C 61.47%;	H 3.83%;	N 10.56%;	S 12.08%

When this compound was heated at 260°C for 15 minutes it thermoset to form a hard polymer.

A 1 to 2 molar ratio of the N-cyanosulfonamide and cyanamide of Jeffamine AP-22 were refluxed in a methanol-ethyl acetate solution for four hours to make a NCNS-12J laminating varnish at 50% concentration. A Torsional Braid curing study was carried out with this laminating varnish. After a 45 minute cure at 204°C the Tg was 232°C. This cure was followed by a 30 minute cure at 232°C and the Tg increased to 285°C. It was concluded that NCNS-12J resin was very similar to NCNS-12M resin with respect to the rate of cure and ultimate glass transition temperature achieved.

A 181E glass prepreg was prepared, dried at 158°F for one hour and B-staged for 15 minutes at 194°F. Fourteen plies were laid up and press laminated at 350°F/1.5 hour-400°F/1 hour at 600 psi. After a 400°F post cure the laminate was found to have an interlaminar shear strength of 45 MPa at 375°F. It was concluded that high strength laminates could be prepared from NCNS-12J resin that had economic advantages. In addition to having a lower raw material cost NCNS-12J resin in the uncured state had a lower melting point which might facilitate ease of processing.

A HT-S unidirectional graphite fiber laminate I-24A-15A, Table 37 was prepared from the NCNS-12J resin for evaluation of humidity-temperature resistance. The 350°F interlaminar shear strength after humidity aging was 44 MPa which was equivalent to the strength obtained with NCNS-12M/ graphite fiber laminates after the same exposure test.

2.2.2 NCNS Resins Prepared from 2,4-Bis(p-aminobenzyl)aniline

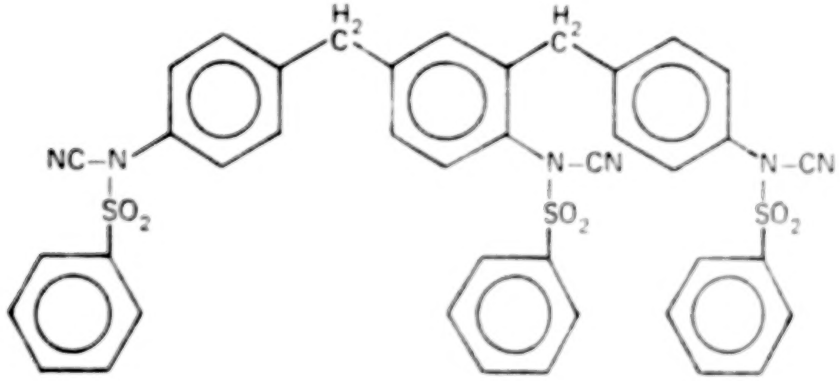
The good properties and humidity resistance of Jeffamine based NCNS resin/ graphite fiber laminates provided a rationale for evaluating NCNS resins prepared from higher concentrations of polymethylene polyphenylamines. The mixture of polymethylene polyphenylamines sold by Dupont as BABA or 2,4 bis(p-aminobenzyl)aniline was used for this investigation (See Table 4, Figures 6 and 7).

Synthesis work was focused on developing a preparative method for making the N-cyanosulfonamide compound of BABA in high yield and purity. BABA in 16/84 water/acetone-sodium bicarbonate slurry was reacted with 5% excess cyanogen chloride at 0°C for 3 1/2 hours. The reaction mixture was then diluted with additional acetone and a stoichiometric equivalent of benzenesulfonyl chloride was added to the mixture at 0°C. A stoichiometric equivalent of triethylamine was then slowly added to the stirred mixture at 0°C over a one hour period. An exotherm occurred during this addition but the reaction temperature was not allowed to increase above 2°C. The reaction mixture was stirred over a 21 hour period during which time the temperature slowly increased to 23°C. The sodium chloride and triethylamine hydrochloride salts were allowed to settle in a lower layer and the top layer containing the product in acetone was removed and added slowly to a six fold excess of rapidly stirred ice water. The precipitated product was filtered off, washed with water, and dried at 60°C/0.1 mm to give a 98.5% yield of the N-cya osulfonamide melting range 75-85°C, gel time 5 minutes at 250°C.

Found	C	62.00%;	H	4.28%;	N	9.96%;	S 11.32%
Theory	C	61.64%;	H	3.78%;	N	10.52%;	S 12.04%

A Torsional Braid curing study was carried out on an ethylene dichloride/ethanol solution of the N-cyanosulfonamide. At a curing temperature of 455°F the modulus increased for 30 minutes and reached a plateau. The Tg was then determined and found to be 275°C. Differential Scanning Calorimetry showed that the heat of polymerization was 60-63 cal/g.

The N-cyanosulfonamide of BABA, although a mixture, for simplicity was assumed to consist entirely of the following molecular structure containing 3 N-cyanosulfonamide groups. The theoretical molecular weight was 798 and



equivalent weight 266. It was reacted with three different levels of MBPC monomer so that for each N-cyanosulfonamide group there would be two, three, and four equivalents of primary (-N-CN) cyanamide present.
H

These resins for purposes of identification were designated as NCNS-12P, NCNS-13P and NCNS-14P resins respectively.

These compositions were prepared and Differential Scanning Calorimetry runs Figures 28, 29, and 30 carried out on the dried resins. Endothermic melting points increased from 61°C for NCNS-12P resin to a high of 109°C for NCNS-14P resin. The initial polymerization exotherms peaking from 143°C to 153°C increased from 43 cal/g for NCNS-12P resin to a high of 53 cal/g for NCNS-14P resin. An intermediate polymerization exotherm of 48 cal/g was observed for NCNS-13P resin. At a temperature range of 250 to 258°C NCNS-12P and NCNS-13P resins showed a second polymerization exotherm of 4 to 5 cal/g which was not observed with NCNS-14P.

Several advantages of the BABA N-cyanosulfonamide compound over MBSPC in NCNS resins were observed, namely:

Lower raw material costs.

Room temperature solubility in a variety of commercially available alcohols, ethers, esters, ketones and chlorinated solvents suitable for laminating varnish preparation.

Improved tack, body and drape of prepregs at higher concentrations of MBPC.

Laminates of increased mechanical strength and lower thermal expansion rates after humidity aging tests.

Table 38 shows three different solvents employed for preparing NCNS-13P resin/181E glass cloth prepregs and press laminates. In runs no. I-25R-26 and I-25R-58 laminates with 400°F short beam shear strengths of 69 MPa were prepared. The latter laminate, Figure 31 had a low Z-axis thermal expansion up to a temperature of 265°C and a final irreversible expansion at 315°C. This high temperature performance exceeded that obtainable with the NCNS-12M resin.

The first BABA based NCNS/graphite fiber laminates prepared for evaluation were made with NCNS-12P resin. In Table 39 in both laminates I-24A-50 and I-24A-50A the initial 350°F short beam strengths were in the 80 to 90 MPa range when the laminate was post cured at 460°F for only four hours or for 60 hours. Thermal Mechanical Analysis expansion of the Z-axis of these laminates however showed that the Tg of the laminate increased from 248°C to 278°C when the post cure was extended to 60 hours.

The retention of initial 350°F short beam shear strengths after 24 and 96 hour water boils was evaluated. Laminate I-24A-50A given the 60 hour post cure retained 80% of its initial strength after 24 hours of water boil and 59% after 96 hours of water boil. These strength retentions after water boil were better than those obtained with laminate I-24A-50 given the shorter post cure. Even though the resin content of laminate I-24A-50A was higher than that of I-24A-50 it absorbed slightly less water during water boil and this result again was probably due to the longer post cure given I-24A-50A which resulted in a higher crosslink density.

The retention of 350°F short beam shear strength after water boil was better in those graphite fiber laminates containing NCNS-12P resin than it was with NCNS-12M resin or NCNS-12J resin. Data confirming this conclusion are shown in Table 40 for graphite laminates I-22F-145, I-24A-15 and I-24A-50 which had similar press laminating and post curing conditions.

2.2.3 Humidity-Temperature Resistance of NCNS-12P and NCNS-13P Resins

Short beam shear samples of NCNS-12P laminates I-24A-50 and I-24A-50A were given humidity aging tests. The data in Table 42 show that after exposure the 350°F interlaminar shear strengths were 44 MPa and 47 MPa respectively thereby confirming that the humidity resistance of NCNS-12P resin increased with increasing time of post cure.

A NCNS-13P/unidirectional HT-S graphite fiber laminate I-24A-64A was fabricated and given a four hour post cure at 460°F. Table 42 shows that this laminate had superior water and humidity resistance when compared to either NCNS-12P laminate I-24A-50 or I-24A-50A. After humidity aging the 350°F short beam shear strength was 48 MPa and after 96 hours water boil tests was 55 MPa.

Thermal Mechanical Analyses were carried out on laminates I-24A-50 and I-24A-64A to see if there was a relationship between Tg, thermal expansion rates and humidity aging results. Both of these laminates had been given identical post cures of four hours at 460°F. Figure 32 shows that laminate I-24A-64A with the higher resin content (42.6% vs 27.1% for laminate I-24A-50) predictably had a slightly higher rate of thermal expansion in the Z-axis than I-24A-50 up to a temperature of 225°C. At 225°C the NCNS-12P resin exceeded its glass transition temperature and expanded rapidly whereas laminate I-24A-64A containing NCNS-13P resin maintained the same low rate of thermal expansion up to a temperature of 275°C where its rate of thermal expansion accelerated. The higher Tg and water resistance of NCNS-13P resin were undoubtedly related and this resin formulation was therefore given priority over NCNS-12P resin for future development.

2.2.4 Post Curing Studies

Post curing studies on NCNS-13P resin/graphite fiber laminates were carried out with the objective of obtaining additional enhancement of humidity aging resistance. The concept that a two stage post cure would yield an improved laminate was partially based on the observation that a fast heat up rate through the 400°F temperature range generated as much as 53 cal/g of heat of polymerization (see Figure 29). If sufficient time was not allowed for this heat of polymerization to dissipate the internal temperature of a thick graphite fiber laminate could theoretically exceed the decomposition temperature of the cured resin during post cure. Additional evidence that a two stage post cure would enhance humidity aging resistance was provided by the experience with NCNS-12M/HT-S graphite fiber laminate I-24A-79, Table 25 wherein the 350°F interlaminar shear strength after humidity aging increased when a 48 hour post cure comprising a second stage 450°F/24 hour cure was used.

Laminate I-24A-105, Table 41 of 30% resin content and 63% fiber volume was fabricated and given a two stage post cure of 10 hours at 400°F and 10 hours at 450°F. This laminate had a 350°F short beam shear strength of 78 MPa. When the thermal expansion in the Z-axis was measured on the Thermal Mechanical Analyzer it was found that it had a lower degree of expansion than a NCNS-13P/HT-S graphite fiber laminate which had been given a single stage 450°F post cure. A comparison of these two thermal expansion curves is shown in Figure 33. The difference in thermal expansion of the two laminates became quite pronounced at temperatures above 225°C.

Short beam shear samples of laminate I-24A-105 were humidity aged and their interlaminar shear strengths were measured at both 300°F and 350°F. The data in Table 42 show that 68% of the original 350°F interlaminar shear strength was retained.

The interlaminar shear strength of the humidity aged samples increased from 53 MPa to 68 MPa when the test temperature was decreased from 350°F to 300°F. A Thermal Mechanical Analysis measurement of the Z-axis thermal expansion of laminate I-24A-105 after humidity aging, shown in Figure 35, revealed that the laminate passed through a glass transition temperature at approximately 180°C. This indicated that humidity-temperature resistance was limited in this sample to a temperature of approximately 320°F.

An additional laminate I-24A-150A containing 14 plies instead of the 10 plies in I-24A-150 was prepared from the same prepreg and given an identical two stage post cure. Short beam shear samples of laminates I-24A-76B, I-24A-105 and I-24A-105A were humidity aged and the gain in weight due to water absorption was evaluated at one week intervals until saturation was achieved. The data in Table 41 showed that the two laminates given the two stage post cure regardless of thickness absorbed about 10% less water than laminate I-24A-76B with a one stage post cure.

2.2.5 Comparative Humidity Resistance of Narmco 5208 and Hexcel F-178 Resins

In order to further insure that a valid comparative standard for the humidity aging resistance of NCNS/graphite fiber laminates was obtained Narmco 5208/Thornel 300 prepreg was purchased and immediately autoclave processed according to manufacturer's instructions, i.e.

Vacuum Bag-Autoclave Conditions

1. Heat to 275°F in 40 minutes with full vacuum.
2. Maintain 275°F for one hour and apply 100 psi pressure.
3. Heat to 355°F in 16 minutes and cure for two hours.

A 25 ply laminate was processed without difficulty with a 30% resin content, 65% fiber volume and zero void content (see Table 42). It was given the recommended 400°F/4 hour post cure and had a 350°F short beam shear strength of 59 MPa. After humidity aging the 350°F short beam shear strength was 38 MPa or considerably lower than 53 MPa observed with NCNS-13P/graphite fiber laminate I-24A-105 after humidity aging.

Hexcel's F-178 bismaleimide/T-300 graphite prepreg was then purchased and immediately vacuum bag-autoclaved acccording to Manufacturer's Instructions, i.e.

Vacuum Bag Autoclave Conditions

1. Apply 2" vacuum and heat from R.T. to 270°F in 30 minutes.
2. Apply full vacuum and 100 psi pressure.
3. Heat from 270°F to 350°F in 15 minutes.
4. Cure for two hours at 350°F/100 psi/full vacuum.

An 18 ply laminate I-24A-97 was prepared that was given a two stage post cure of 400°F/4 hours -475°F/10 hours. The laminate of 32% resin content and 65% fiber volume was void free and had a 350°F short beam shear strength of 68 MPa (see Table 42). After humidity aging the 350°F short beam shear strength was 33 MPa (49% retention of original strength).

It was concluded that the NCNS resins offered a significant increase in humidity resistance over the competitive F-178 and 5208 resin systems.

The thermal expansions in the Z-axis of NCNS-13P, NCNS-12M, Narmco 5208 and Hexcel F-178 laminates were compared in Figure 35. The highest expansion was shown by 5208 and the least by F-178. This was expected since maleimide resins have a higher use temperature than epoxy resins. NCNS-13P resin had a thermal expansion only slightly higher than that of F-178 but it had been given a post cure at 450°F vs. 475°F for F-178.

2.2.6 NCNS-14P Resin

The trend towards increased humidity aging resistance in the NCNS resins tabulated in Table 42 as one progressed in composition from NCNS-12P to NCNS-13P suggested that NCNS-14P might have even greater resistance to attack by water. NCNS-14P resin was found to have a higher melting point and shorter gelation time than either NCNS-12P or NCNS-13P resin. Despite processing difficulties void free NCNS-14P/HT-S unidirectional graphite laminates were compression molded at 350°F/600 psi/1 hour and post cured with various temperature regimes. Laminate I-24A-103A with an initial 400°F short beam shear strength of 75 MPa was oxidatively aged at 400°F and short beam shear samples were periodically removed for retention of 400°F interlaminar shear strength. Figure 36 shows that there was no change in strength with 1000 hours of aging. Humidity aging of short beam shear samples were carried out and the highest interlaminar shear strength at 350°F observed after exposure was 50 MPa. These samples did not fail by a shear mode but bent in compression failure. It was concluded that the NCNS-13P resin formulation was superior to the NCNS-14P resin in both humidity temperature resistance and processability. To obtain corroboration of these results with NCNS-13P and NCNS-14P resins two pounds of NCNS-13P resin and a NCNS-14P/HT-S unidirectional graphite fiber laminate of 10" x 10" x 1/8" dimensions were sent to the NASA Langley Research Center for testing.

2.2.7 Storage Stability of NCNS-13P Resin Prepreg

A sample of the tacky, drapable prepreg used to fabricate laminate I-24A-105 was stored in a polyethylene bag in the freezer for a period of 30 days. This prepreg was then given the standard B-staging of 90°C/15 minutes and press lamination of 350-400°F/2 hours. After a 400°F/10 hour - 460°F/10 hour post cure a laminate of 66% fiber volume, 26.6% resin content and a 350°F short beam shear strength of 69 MPa was produced. Short beam shear samples were then humidity aged and the 350°F short beam shear strength was 46 MPa. This experiment demonstrated that the NCNS-13P prepregs retained processability and properties upon storage for at least a month.

2.2.8 Vacuum Bag-Autoclave Processing of NCNS-13P Resin

NCNS-13P resin/AS graphite fiber prepregs were prepared from laminating varnishes made with a 60/40 methanol/ethyl acetate solvent mixture and with methyl ethyl ketone or acetone. The prepregs were laid up while still tacky and drapable and placed in a nylon vacuum bag for processing. Commercially feasible autoclave heat up rates of 5°F/minute were employed. Table 43 shows two different 400°F vacuum bag-autoclave processes cycles that were found to be suitable for producing laminates with 1% or less void contents and with high 400°F interlaminar shear strengths. The first processing cycle used in runs no. I-24A-133 and I-27U-11 employed a 30 minute hold at 212°F under vacuum to remove the solvent before application of pressure at 257°F. The 400°F interlaminar shear strengths of these laminates were 61 MPa and 57 MPa respectively. Higher interlaminar shear strengths at 400°F were obtained by the second processing cycle used in runs no. I-27U-21, I-27U-22, and I-27U-28 that held the temperature at 140°F under vacuum for one hour to remove solvent residues before applying autoclave pressure at 239°F. In these runs the 400°F interlaminar shear strength increased from 67 MPa to 86 MPa as the resin flow on the bleeder cloths increased from 2 to 6% respectively. The properties of these laminates were equivalent to those achieved by press laminating at higher pressures.

2.2.9 NCNS-13P Resin Pilot Plant Batch 7/7/1002

Laboratory evaluations confirmed that the NCNS-13P resin had the best balance of processing characteristics and strength properties after humidity aging of any of the various NCNS resin formulations prepared. In order to provide sufficient NCNS-13P resin for larger scale evaluations one hundred pounds of NCNS-13P resin, batch no. 7/7/1002 was prepared in the P/A Division Pilot Plant. Table 44 shows the data from the initial evaluation of this resin. An unidirectional AS graphite fiber laminate was fabricated that had a 65% fiber volume and was void free. At 400°F the flexural strength was 1640 MPa, flexural modulus 119,000 MPa and short beam shear strength 79 MPa. This 6" x 6" x 1/8" laminate was cut up into short beam shear samples for oxidative aging at 450°F for 3000 hours. Figure 37 shows that there was no loss in 400°F interlaminar shear strength over this oxidative aging period. It was concluded that NCNS-13P resin was a candidate for +10,000 hours performance at 450°F.

2.2.10 Char Contents, Burn Tests, Smoke and Toxic Gas Emissions

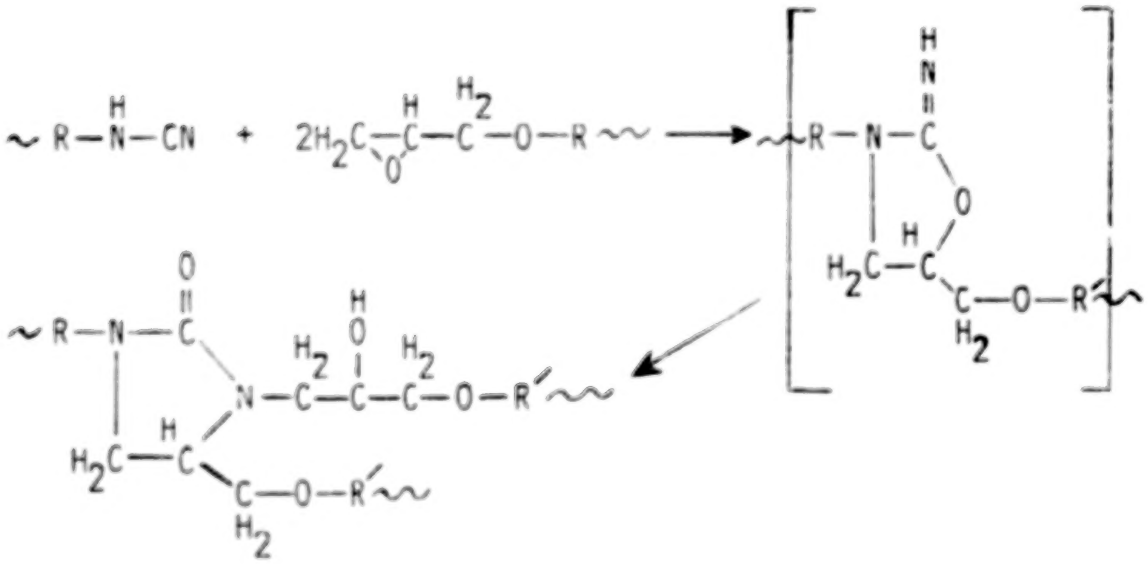
NCNS-13P resin was B-staged for 30 minutes at 110°C and compression molded at 300-350°F/300 psi/1 hour. The molded plaque was then given a 452°F/7 hour - 460°F/8 hour post cure. A Thermogravimetric Analysis shown in Figure 24 was carried out under nitrogen at a heating rate of 10°C/minute. Figure 24 shows that the NCNS-13P resin lost less weight than NCNS-12M resin between the temperatures of 100 to 900°C. The NCNS-13P resin at 900°C left a char of 64% vs. 59% for NCNS-12M resin. These high char values for the NCNS resins were exceptional when compared to other known fire retardant, low smoke generating resins.[13]

NCNS-13P/181E glass cloth laminate I-24A-119 of 23% resin content was tested in Federal Aviation Vertical Burn Test 25.853A. Table 45 compares the data from this laminate with that from a NCNS-12M/181E glass cloth laminate with the same resin content. Neither of these laminates would burn in 100% oxygen (LOI 100). After removal of the flame the samples ceased burning in 6 to 8 seconds and the burn lengths were 1.1 to 1.2 inches. These laminates were also tested in the American Instrument Company Smoke Density Chamber under flaming conditions. The chamber was equipped with Draeger Tubes for the quantitative analysis of toxic gases CO, HCN, SO_2 and NO_x (mixed nitrogen oxides). Three samples of each laminate, i.e., I-24A-119 and I-24A-95 were tested. Table 45 shows that the smoke densities and toxic gases evolved from all of the samples regardless of the NCNS resin composition were extremely low and comparable to those values previously observed only with polyimides and exotic high temperature polymers. Carbon monoxide was the most prevalent toxic gas generated while HCN, SO_2 and NO_x concentrations which were usually below 10 ppm were at such a low level that they should not prevent the use of the NCNS resins in aircraft passenger compartments. The NCNS-12M laminate having the highest concentration of N-cyanosulfonamide groups, after 20 minutes of exposure to flame yielded the highest concentrations of toxic gases in this study. In the NCNS-13P laminate where the N-cyanosulfonamide group concentration was lowest and the aromatic cyanamide group concentration the highest the HCN, SO_2, and NO_x concentrations were 5 ppm or less.

Another NCNS-13P/181E glass cloth laminate I-25R-26 was prepared at 24.6% resin content in order to confirm the absolute level of smoke that it would generate under flaming conditions. Figure 38 showed that the corrected specific optical density of the smoke never exceeded a Dm of 29 during the 20 minutes time period of the test and it required 7 minutes time for the Ds to exceed a value of 16 which the FAA considers the level at which exit signs in an airplane could be obscured. Figure 39 shows that a NCNS-13P/unidirectional AS graphite fiber laminate of 32.3% resin content predictably gave higher smoke levels. In this case after 15 minutes in the flaming mode the corrected Dm reached 57. After 20 minutes in the flame the laminate was swollen and had lost 7.4% of its weight (22.9% of its resin) but no graphite fibers were exposed and the laminate had not fragmented.

2.3 NCNS Resins Curable at 250°F

A number of experiments were carried out to determine if BABA based NCNS resins could be formulated with epoxy resins to yield 250°F curable systems with physical properties better than the commercially available epoxies. In preliminary trials NCNS-12P resin was blended with 20% by weight ARALDITE 6005, a low viscosity i.e., 7,000-10,000 cps compound containing mainly the bisglycidyl ether of bisphenol-A. It was projected that cyanamide groups in the NCNS resin would react with epoxy groups by the following reaction sequence.



In run no. I-24M-98, 16.67 g of NCNS-12P powder and 3.79 g of ARALDITE 6005 (189 epoxy equivalent) were dissolved in acetone and the solution evaporated to remove the solvent. The isolated resin, NCNS-12PE, was a gum that formed a clear liquid at 35°C and gelled at 100°C in 9 minutes. The Differential Scanning Calorimeter run in Figure 40 showed that at a heating rate of 10°C/ minute polymerization commenced at 99°C, peaked at 125°C, and terminated at 184°C. A slower heating rate of 2.5°C/minute found polymerization starting at 82°C, peaking at 106°C and terminating around 124°C. When these DSC curves were compared to that of NCNS-12P resin the effect of the epoxy resin in lowering the polymerization temperature of the NCNS resin was apparent.

Infra-red spectra were run on the NCNS-12PE resin before and after curing and the nitrile group absorption peak at 4.4 microns was found to disappear along with the epoxy group at 10.9 microns when the resin was heated above 100°C.

NCNS-13P resin was dissolved in acetone along with 20% by weight ARALDITE 6005, (weight per epoxy group 175). This solution of NCNS-13PE resin was submitted for Torsional Braid curing studies. The braids were cured at both 250°F and 450°F temperatures and the glass transition temperature of the resin cured at either temperature was found to be 275-280°C. In Figure 41 was plotted the increase in modulus vs. time for both cure temperatures. At a cure temperature of 250°F the modulus increased for 15 minutes whereas a 450°F cure temperature the cure was completed in 2 to 3 minutes.

2.3.1 Laminates of NCNS-13PE Resin Prepared from ARALDITE 6005

A 50% acetone solution of this NCNS-13PE resin was used to prepare a 181E glass prepreg. The prepreg was B-staged at 175°F for 30 minutes and then 15 plies were press laminated at 250°F/600 psi/30 minutes. A well consolidated laminate was produced. This laminate was given a 400°F/10 hour - 450°F/10 hour post cure and appeared to survive the 450°F cure temperature as well as the unmodified NCNS-13P resin. Laminates were then prepared at both 250°F and 350°F molding temperatures in order to find out whether molding at the lower 250°F temperature resulted in compromising the strength characteristics of the laminates.

The results of this investigation are given in Table 46. The data showed that the 250°F molding temperature resulted in producing laminates with higher interlaminar shear strengths than the 350°F molding temperature. A short 400°F post cure of 3 hours gave a laminate with excellent 300°F short beam shear strength. When the laminate was molded at 250°F and given a 400°F/10 hour - 450°F/10 hour post cure the 400°F short beam shear strength approached that of the NCNS-13P resin without epoxy.

A 181E glass fabric prepreg of NCNS-13PE resin was stored for 35 days in a polyethylene bag at room temperature. After storage 14 plies were B-staged for 30 minutes at 80°C and then press laminated at 250°F/600 psi for 30 minutes. After a three hour post cure at 425°F this laminate had a 350°F short beam shear strength of 59 MPa vs. 65 MPa achieved with freshly prepared prepreg under the identical processing and post curing conditions. The storage stability of the NCNS-13PE resin thus appeared to be relatively good when it was considered that epoxy prepregs are normally stored under refrigeration conditions.

The NCNS-13PE resin was evaluated for thermal and humidity resistance at elevated temperatures. The characterization and performance properties of this laminate are given in Table 47. The data show that a high density, negligible void, 67% fiber volume laminate was prepared. At 350°F its initial interlaminar shear strength of 59 MPa was approximately 75% of that of NCNS-13P/graphite fiber laminates. Short beam shear samples of I-24A-139 were humidity aged and the retention of 350°F interlaminar shear strength over this exposure period was 65%. At 300°F the interlaminar shear strength after humidity aging was 64 MPa which indicated negligible loss in strength at this temperature.

The Thermal Mechanical Analysis run shown in Figure 42 compared the Z-axis expansion of this laminate I-24A-139 prepared from NCNS-13PE resin vs. I-24A-105A prepared from NCNS-13P resin. It was observed that laminate I-24A-139 had a slightly higher thermal expansion and showed irreversible expansion at 300°C at a 20°C lower temperature than I-24A-105A.

Short beam shear samples were oxidatively aged in a forced draft air oven at 350°F for 2500 hours. Figure 43 shows that the 350°F interlaminar shear strength increased over this period to 67 MPa with no evidence of oxidative degradation detected.

NCNS-13PE/181E glass cloth laminates of 23.5% and 24.6% resin contents were submitted for smoke density determinations under flaming conditions. Figure 44 shows that the maximum specific optical densities were 48 and 105 respectively. It was concluded that the use of 20% by weight of ARALDITE 6005 epoxy in the NCNS-13PE resin doubled the quantity of smoke normally obtained with NCNS resin glass cloth laminates.

2.3.2 Laminates of NCNS-13PE Resin Prepared from ARALDITE 6010

The ARALDITE 6005 resin used in this work contained some monofunctional epoxy which lowered its viscosity. It was thought possible that this monofunctionality could also decrease the Tg of the NCNS-13PE resin prepared from the 6005 epoxy. In order to examine this possibility ARALDITE 6010, viscosity 12,000-16,000 cps, epoxy value 0.53 eq/100 g, a difunctional diglycidyl ether of bisphenol-A, was used with NCNS-13P resin to prepare several laminates for evaluation.

The substitution of 6010 for 6005 at the 20% by weight concentration with NCNS-13P resin required no change in processing technique. A 181E glass cloth laminate, I-25R-8A was prepared at 250°F/600 psi and given a 425°F/7 hour - 460°F/2 hour post cure. The laminate had a resin content of 25% and a room temperature short beam shear strength of 89 MPa. Figure 45 shows a plot of short beam shear strength vs. temperature. The short beam shear strength showed little change up to 300°F and at 350°F approximately 75% of the room temperature strength was retained. At 400°F only 50% of the room temperature strength was retained. The Z-axis expansion vs. temperature was determined on this laminate with the Thermal Mechanical Analyzer. Figure 46 shows that the rate of expansion was linear up to a temperature of approximately 175°C. Between 175°C and 200°C the rate of expansion accelerated and at 265°C was irreversible. The change in expansion rate above 175°C (347°F) correlated with the drop-off of interlaminar shear strength at this temperature which was shown in Figure 45.

2.3.3 Effect of Glycidylated Compound Structural Variations

With the demonstration of a 250°F cure system the reactions of a variety of other glycidylated compounds with NCNS-13P resin were examined with the objective of achieving improved processability in the prepregs without a significant compromise in the high temperature strength of the laminates.

The structures of the epoxies selected for this investigation are given in Table 48. The processing conditions and physical properties of both 181E glass cloth and unidirectional AS graphite fiber laminates are given in Table 49. In run no. I-25R-36 20% by weight of low molecular weight DGEBA (6010) and 80% NCNS-13P resin on 181E glass cloth gave a laminate with a 400°F interlaminar strength of 57 MPa. The freshly prepared prepreg was tacky and drapable but gave evidence of having poor storage stability at room temperature as shown in run no. I-25R-37A where the prepreg I-25R-36 was stored at room temperature for 24 hours before processing. Resin flow during lamination decreased and the 400°F interlaminar shear strength of this laminate decreased to 36 MPa.

In run no. I-25R-46A, 20% by weight of high molecular weight glycidyl terminated GT 7014 and 80% NCNS-13P resin were used to prepare a 181E glass cloth prepreg. GT 7014 contained only 25% of the epoxy functionality present in runs no. I-25R-36 and I-25R-37A and therefore might be anticipated to be less reactive at room temperature and give prepregs with greater shelf stability. In both runs I-25R-46A and in run I-25R-50C where unidirectional AS graphite fiber prepreg was prepared it was found that B-staging conditions as high as 90°C/1 hour could be employed while still obtaining adequate melt flow during press lamination. It was anticipated therefore that the prepregs from this resin system would have improved shelf stability.

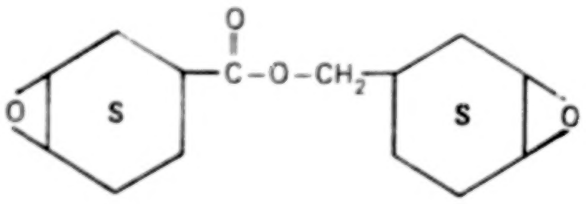
In run no. I-25R-57A, 10% by weight of MY 720 (tetraglycidylated 4,4'-methylene dianiline) was blended with NCNS-13P resin and used to prepare an unidirectional AS graphite fiber laminate that had a 350°F interlaminar shear strength of 103 MPa. The high strength of this laminate encouraged further exploration into the performance of NCNS-13P-epoxy resins which contained a low percentage weight of liquid epoxy of high glycidyl functionality. In run no. I-25R-60 the triglycidylated p-aminophenol (0500) (1500 to 5000 cps viscosity) at 10% concentration was reacted with NCNS-13P resin. The 181E glass cloth laminate during processing gave high melt flow. After post curing at 400°F/10 hours the laminate had a 400°F interlaminar shear strength of 64 MPa. The low viscosity of ARALDITE 0500 and the high melt flow obtained after extensive heating of the prepreg at 75°C indicated that NCNS-13P-0500 epoxy resin had potential for developing storage stable, tacky, solventless prepregs.

In run no. I-25R-61 the glycidylated cresol Novolac ECN 1273 at 10% concentration was blended with 90% by weight of NCNS-13P resin. The 181E glass cloth laminate during processing gave high melt flow. The laminate had an interlaminar shear strength of 58 MPa. Prepreg tack and drape were deficient because both ECN 1273 and NCNS-13P resins were solids at room temperature.

The Z-axis thermal expansions of these 181E glass laminates were measured on the Thermal Mechanical Analyzer and plotted in Figure 46. The NCNS-13P-0500 laminate and NCNS-13P-ECN 1273 laminate had the lowest coefficients of thermal expansion. From these curves the glass transition temperatures of the polymers were estimated to be approximately 210°C.

2.3.4 NCNS-13PE Resin Prepared from Cycloaliphatic Epoxies

The evaluations of various ARALDITE epoxy resin blends with NCNS-13P resin were continued with the additional objective of achieving a solventless, melt prepreggable composition for graphite fiber laminates. It was observed that ARALDITE CY 179 had a high compatibility and reduced reactivity with NCNS-13P resin compared to epoxy resins containing glycidyl groups. CY 179 was a cycloaliphatic resin with two cyclohexene oxide groups of low reactivity, i.e., 3,4-epoxycyclohexylmethyl,3,4-epoxycyclohexanecarboxylate.



CY 179, 10% by weight was dissolved in acetone with 90% by weight of NCNS-13P. The acetone solution was evaporated to dryness. The resinous mixture melted at approximately 40°C and formed a clear low viscosity liquid which at a temperature of 60°C remained fluid for several hours. The gelation time at temperatures between 80°C and 110°C was measured on a hot stage and the resulting data were plotted in Figure 47. The gelation time varied from 10 minutes at 110°C to approximately one hour at 80°C. When the CY 179 concentration was reduced from 10% to 5% concentration the melting point of the resin remained approximately the same but the gelation time at 80°C was increased to 95 minutes.

In further characterization studies on 10% CY 179-90% NCNS-13P resin blends Differential Scanning Calorimetry run, Figure 48 showed that at a heating rate of 10°C/minute a polymerization exotherm initiated at 99°C, peaked at 140°C and terminated at 189°C. A second exotherm peaking at 236°C was observed which was believed due to a final N-cyanosulfonamide group polymerization. In a Torsional Braid curing study at 400°F the modulus increased rapidly for the first twenty minutes but after 40 minutes remained constant. Raising the temperature above 400°F showed that the resin achieved a glass transition temperature of 298°C. The CY 179-NCNS-13P resin in general cured faster at a given temperature than NCNS-13P resin but not as fast as glycidyl epoxy compounds with NCNS-13P resin.

NCNS-13P resin was dissolved in acetone with 5% and 10% by weight of CY 179 and the solutions were used to prepare unidirectional AS graphite fiber prepregs. After the acetone was removed by evaporation the solventless prepreg remained drapable and tacky particularly at a 10% CY 179 concentration.

A series of vacuum bag-autoclave trials were carried out.

In Table 50 with 10% by weight of CY 179 present in runs I-25R-89 and I-25R-106 it was found that autoclave pressure could be applied at 60°C after holding vacuum on the lay-up at room temperature. Better results were obtained with 5% CY 179 concentrations when the pressure was applied at 90°C. The 350°F interlaminar shear strength ranged between 48 MPa and 61 MPa with 10% CY 179 present. Short beam shear samples of laminate I-25R-89 when humidity aged showed no deterioration of 350°F interlaminar shear strength. In runs no. I-25R-98, 100, and 111 the interlaminar shear strengths at 350°F were as high as 65 MPa with 5% CY 179 present. In run no. I-25R-100 the retention of 350°F interlaminar shear strength after 30 day humidity exposure was 72%. These results indicated that higher concentrations of CY 179 favored better humidity resistance as well as better tack and drape of the prepregs.

Laminates I-25R-85 and I-25R-100 along with a NCNS-13P/graphite laminate I-24A-133 were submitted for Thermal Mechanical Analysis. A plot of their Z-axis thermal expansions in Figure 49 showed almost identical expansions up to a temperature of 250°C regardless of the concentration of CY 179 and the fact that laminate I-24A-133 was post cured at 460°F and the other laminates at 400°F. Above 250°C both laminates containing CY 179 showed extreme thermal expansions whereas laminate I-24A-133 with no CY 179 did not undergo extreme thermal expansion until a temperature of approximately 290°C was reached. The glass transition temperatures of these resins were thought to be 255°C and 290°C respectively - the use of 5 to 10% CY 179 in NCNS-13P causing about a 35°C degree depression in the glass transition temperature of NCNS-13P resin.

2.3.5 Post Curing Studies on NCNS-13PE Resins

The effect of post curing temperatures on the interlaminar shear strengths of various NCNS-13PE laminates was evaluated and the data are shown in Table 51. The epoxy content was maintained at the 10% weight level and three different ARALDITE epoxy resins were compared, i.e., epoxy cresol Novolac 1273, MY 720 and CY 179. The data show that a post cure of 400°F gave NCNS-13PE laminates with the highest interlaminar shear strengths. Raising the post cure temperature to 425°F caused a deterioration in the 350°F interlaminar shear strength of laminate I-25R-100 containing the cycloaliphatic resin CY 179. A 460°F post cure of this laminate resulted in heat distortion. Laminates I-25R-61 and I-25R-53 containing ECN 1273 and MY 720 respectively survived the 460°F post cures but their interlaminar shear strengths were decreased by this cure temperature when compared to strengths obtained by post curing at 400°F.

In conclusion the NCNS-13PE blends gave prepregs with tack and drape in the solvent free state. These prepregs were fabricated by 250°F vacuum bag-autoclave processes into void free high strength graphite fiber laminates with humidity resistance and improved fire resistance compared to epoxies.

2.4 NCNS Resins Prepared from other Diamines[14]

An effort was made to prepare NCNS resins with lower melting points, improved prepreg tack and drape, improved humidity aging resistance and higher char values than those derived from 4,4'-methylene dianiline or polymethylene polyphenylamine precursors. Various other diamines were investigated as NCNS resin precursors in order to evaluate the influence of molecular structure on resin performance.

2.4.1 NCNS Resin Prepared from 5(6)-Amino-1-(4'-aminophenyl)-1,3,3-trimethylindane

An attempt was made to prepare a NCNS resin with a low melting point from an isomeric mixture of 5(6)-amino-1-(4'-aminophenyl)1,3,3-trimethylindane (DAPI) which was liquid at room temperature. It was converted into the bis N-cyanosulfonamide derivative by the conventional reaction with benzenesulfonyl chloride and cyanogen chloride. A 73.5% yield of the product was isolated:

Found	C 64.19%;	H 4.98%;	N 9.20%
Theory	C 64.41%;	H 4.73%;	N 9.39%

DAPI was reacted with CNCl in $NaHCO_3$ methanol slurry to yield the biscyanamide in 99.2% yield.

Found	C 73.89%;	H 6.60%;	N 17.33%
Theory	C 75.92%;	H 6.37%;	N 17.71%

The biscyanamide was reacted with the bis N-cyanosulfonamide of DAPI by refluxing the two monomers in acetone/tetrahydrofuran solvent mixture. The NCNS-12 DAPI resin was isolated by precipitating it into water and drying under vacuum at 40°C. This resin melted at 65°C and thermoset rapidly upon heating above 130°C. It was soluble at high concentrations in ethylene dichloride, chloroform and 80/20 THF/ethyl acetate solvents.

The THF/ethyl acetate laminating varnish was submitted for Torsional Braid curing studies. After 40 minutes of curing at 400°F the modulus reached a maximum level and upon further heating a Tg of 307°C was observed. This Tg was about 40°C higher than that achieved with the corresponding 4,4'-methylene dianiline based NCNS resin.

A 181E glass fabric reinforced laminate was prepared and evaluated and the processing conditions and physical properties are given in Table 52. Higher melt flow during press laminating was noted with DAPI resin than with MDA resin. The DAPI laminate was void free and had 400°F physical properties within the anticipated strength range previously established for 181E glass laminates of the NCNS-12M resin.

A unidirectional HT-S graphite laminate was prepared from the NCNS-12 DAPI resin in 80/20 THF/ethyl acetate. The processing conditions and physical properties of this laminate are given in Table 52. The 400°F flexural strength properties of this laminate approximated those previously observed for NCNS unidirectional HT-S fiber laminates. Humidity aging tests were carried out on short beam shear samples. After humidity exposure only 30% of the initial 350°F short beam shear strength was retained.

2.4.2 NCNS Resin Prepared from M-Xylylene Diamine

M-xylylene diamine was reacted with cyanogen chloride in THF at 0-5°C over a 17 hour period. The diamine hydrochloride was filtered off and the THF filtrate was added to ice-water to precipitate the biscyanamide. It was reacted with excess benzenesulfonyl chloride in THF in the presence of triethylamine. This reaction was allowed to proceed at room temperature for 60 hours. The triethylamine hydrochloride was filtered off and the filtrate was vacuum stripped to completely remove the THF. The residue was dissolved in methanol and reprecipitated with water to yield an oil which was dried at 60°C in vacuum. The yield of oily N-cyanosulfonamide was quantitative. This compound at 250°C polymerized in 20 minutes.

Found	C	56.72%;	H	4.30%;	N	11.78%;	S 13.42%
Theory	C	56.64%;	H	3.89%;	N	12.01%;	S 13.75%

A monomeric mixture of one mole of N-cyanosulfonamide and two moles of MBPC was prepared by dissolving the monomers in acetone and quantitatively precipitating the mixture in petroleum ether. This mixture melted at 80°C and thermoset within 10 minutes at 130°C. At 100°C however the gelation period was approximately one hour and this suggested that a solventless melt prepregging technique should be tried due to difficulties in obtaining a stable laminating varnish in various solvents.

The powdered resin was used to impregnate 181E glass fabric at 100°C by the use of slight or "kiss" pressure. The 13 ply press laminate fabricated at 350-400°F/2.5 hours/200 psi was post cured at 435°F for 4 hours. The 400°F flexural strength was 453 MPa and flexural modulus 23,600 MPa. This laminate, however, suffered uneven resin distribution since a number of 400°F short beam shear measurements taken from different areas of the laminate showed the short beam shear strength to vary widely from a value of 14 MPa to 48 MPa.

A HT-S graphite fiber laminate I-24A-9A, Table 37 was fabricated and short beam shear samples were humidity aged. Retention of 350°F short beam shear strength over this humidity exposure cycle was not as high as that achieved with the NCNS-12M resin.

2.4.3 NCNS Resins Based on 2,4-Diaminotoluene

2,4-Diaminotoluene was reacted with cyanogen chloride in a sodium bicarbonate methanol suspension at 0°C. The biscyanamide was isolated in 68% yield for evaluation as a potentially low cost monomer.

Found	C 62.38%;	H 4.63%;	N 32.68%
Theory	C 62.78%;	H 4.68%;	N 32.54%

A portion of this biscyanamide was reacted with two equivalents of benzenesulfonyl chloride to give a 78% yield of the corresponding N-cyanosulfonamide, m.p. 158-159°C.

Found	C 55.55%;	H 3.69%;	N 12.44%;	S 14.11%
Theory	C 55.74%;	H 3.56%;	N 12.38%;	S 14.17%

This compound was found to polymerize to form a hard polymer after heating for 25 minutes at 250°C.

Attempts were made to prepare laminating varnishes by reacting 1/2 molar ratios of the N-cyanosulfonamide and biscyanamide. This monomer mixture was heated in methanol/ethyl acetate, acetone, dioxane, and THF solvents but the N-cyanosulfonamide was not sufficiently soluble to allow the preparation of stable laminating varnishes with resin concentrations in the practical range of 25% or greater.

2.5 Miscellaneous Cyanamide and N-Cyanosulfonamide Monomers

In carrying out the exploratory program to obtaining optimal NCNS resin compositions for composite fabrication the following monomers were also prepared and preliminarily characterized.

2.5.1 Meta Phenylene Biscyanamide

Meta phenylene diamine was reacted at 0°C with cyanogen chloride in a 50/50 methanol/water solution containing excess sodium bicarbonate. The reaction mixture was stirred for 17 hours. The meta phenylene biscyanamide was filtered off and washed with water to remove inorganic salts. The product was then dissolved in cold acetone, treated with charcoal, and the acetone filtrate was added to a large volume of water to reprecipitate the product. The meta phenylene biscyanamide was dried at room temperature at 0.1 mm vacuum, yield 81%. The NMR spectra was consistent with the proposed structure.

Found	C 60.28%;	H 3.63%;	N 34.99%
Theory	C 60.75%;	H 3.82%;	N 35.42%

2.5.2 4-Chloro-m-phenylene Biscyanamide

4-Chloro-m-phenylenediamine was considered as a precursor for preparing NCNS resins with improved humidity resistance. This diamine was reacted with cyanogen chloride in MEK-H_2O-$NaHCO_3$ to give a small yield of the corresponding biscyanamide.

Found	C	49.57%;	H	3.17%;	N	29.70%;	Cl 18.10%
Theory	C	49.89%;	H	2.62%;	N	29.09%;	Cl 18.41%

2.5.3 4,4'-Methylene bis(N-methanesulfonylphenylcyanamide)

MBPC was reacted with excess methanesulfonylchloride in THF solution at room temperature in the presence of triethylamine. After a 16 hour reaction period the triethylamine hydrochloride was filtered off. The filtrate was vacuum stripped to remove the THF and the residue was dissolved in hot acetone and reprecipitated with methanol to give a 51% yield of crude 4,4'-methylene bis(N-methanesulfonylphenylcyanamide), m.p. range 130-140C. At 250°C this compound polymerized in 30 minutes.

Found	C	50.89%;	H	3.96%;	N	14.09%;	S 15.39%
Theory	C	54.82%;	H	4.33%;	N	15.04%;	S 17.22%

2.5.4 4,4'-Methylene bis(N,N'-trifluoromethanesulfonylphenylcyanamide)

Trifluoromethanesulfonyl chloride (0.144 moles) was reacted with 0.076 moles of 4,4'-methylene bisphenylcyanamide in a 90/10 acetone/water solution in the presence of 0.148 moles of sodium carbonate. The reaction mixture was stirred at 0-5°C for 48 hours. Excess solvent was then removed by vacuum stripping and the concentrate was poured into a rapidly stirred saline solution to precipitate the product as an oily gum. It was washed with water and dried under high vacuum at 90°C. The product weighed 34.0 g (94% yield), was an amber colored translucent semi-solid without a distinct melting point. At 40°C it formed a fluid melt and at 250°C it thermoset within 5 minutes.

Found	C	39.84%;	H	2.15%;	N	10.88%;	S	12.01%;	F 21.67%
Theory	C	39.85%;	H	1.97%;	N	10.93%;	S	12.52%;	F 22.25%

An acetone solution of the 4,4'-methylene bis(N,N-trifluoromethanesulfonylphenylcyanamide) was submitted for a Torsional Braid curing study. At a curing temperature of 235°C, the rigidity of the braid increased for 15 minutes. Further heating of the braid showed that the cured polymer had a glass transition temperature of 275°C.

3. CONCLUSIONS - PART III

1. NCNS resins, cured by the addition polymerization of cyanamide groups, were single component systems not requiring catalyst or hardener with excellent long term room temperature stability.

2. NCNS resins could be processed by 400°F. vacuum bag-autoclave molding cycles or rapid, i.e. 3 minute, compression molding cycles.

3. NCNS resins retained high char contents, i.e., >60%, at 900°C. in an inert atmosphere.

4. NCNS laminates completely retained their 400°F. interlaminar shear strength after 450°F./3000 hour oxidative aging cycles.

5. NCNS laminates were non-burning and gave low smoke densities and toxic gas emissions.

6. NCNS/graphite fiber laminates after humidity aging cycles retained 350°F. interlaminar shear strengths better than epoxy and polymaleimide graphite fiber laminates.

7. NCNS resins were compatible and reactive with epoxy resins and gave novel resin alloys.

8. NCNS-epoxy alloys gave prepregs with lower volatile contents and improved tack and drape compared to non-alloyed NCNS resins.

9. NCNS-epoxy alloys had better oxidative stability, humidity resistance and non-burning characteristics than commercially available epoxy resins.

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TABLE I

550°F VACUUM BAG-AUTOCLAVE PROCESSING OF COMPETITIVE POLYIMIDES P-105A, PMR-15, LARC-160M AND LARC-3A

Laminate No.	I-229-28	I-229-128	I-24A-47	I-270-4	I-270-5
Resin	P-105A	LARC-160M	PMR-15	LARC-160M	LARC-160A-3
Reinforcement	12 plies 181E glass cloth, 7" x 8"	12 plies 181E glass cloth, 7" x 8"	14 plies glass cloth 7" x 8" (Ferro Preprog CPI-2237/7781)	24 plies, 6" x 6", Celion 6000	24 plies, 6" x 6", Celion 6000
Prepreg Volatile Content	9%	3.3%	7.3%	21%	23%
B-Staging Conditions	None	120°C/1 hr.	None	None	None
Vacuum Bag-Autoclave Processing Conditions	1) Heat to 390°F in 2 hrs./ full vacuum. 2) Hold 390°F for 2 hrs. 3) Heat to 420°F in 10 mins. and apply 90 psi pressure. 4) Heat to 550°F in 50 mins. and cure for 2 hrs.	1) Heat to 490°F in 85 mins./ full vacuum. 2) Apply 200 psi pressure and heat to 550°F in 12 mins. 3) Cure 2 hrs. @ 550°F.	1) Heat to 400°F in 60 mins./3" vacuum. 2) Hold 400°F for 3 hrs./3" vacuum. 3) Heat to 490°F, apply full vacuum and 100 psi pressure. 4) Heat to 550°F in 8 mins. and cure 1 hr.	1) Heat to 194°F and hold 1 hr. - no vacuum. 2) Apply 2" vacuum and heat to 325°F in 26 mins. 3) Hold 325°F for 3 hrs. 4) Heat to 525°F apply 200 psi pressure. 5) Heat to 550°F and cure 1 hr.	Same as I-270-4
Resin Melt Flow	6.8%	4%	40%	28.5%	7%
Post Cure	575°F/4 hrs.	575°F/4 hrs.	575°F/16 hrs.	575°F/4 hrs.	575°F/4 hrs.
Resin Content	31.3%	29.1%	25.4%	28.3%	29.2%
Fiber Volume	--	--	--	65.2%	64.4%
Void Content	4.6%	0.4%	0.2%	0.6%	zero
500°F Flexural Strength, MPa	480	480	538	--	--
500°F flexural Modulus, MPa	16,800	17,200	22,100	--	--
500°F Short Beam Shear Strength, MPa	44	51	49	49 38 (600°F)	50 37 (600°F)

TABLE 2

NADIMIDE TERMINATED SOLUBLE IMIDE PREPOLYMERS - PROCESSING AND PROPERTIES

Laminate No.	I-22F-98	I-22F-104	I-22F-110	I-22F-113	I-22F-117	I-22F-130
Resin Composition	2 NA/3 CPDA/ 2 BTDA	2 NA/3 CPDA/ 2 BTDA	2 NA/4 CPDA/ 3 BTDA	2 NA/3 CPDA/ 2 BTDA	2 NA/3 CPDA/ 2 BTDA	2 NA/2 CPDA/ 1 BTDA
Reinforcement	4" x 4" 181E glass cloth, 12 plies	7" x 8" 181E glass cloth, 12 plies	4" x 4" 181E glass cloth, 12 plies	7" x 8" HT-S graphite fiber, 11 plies unidirectional	4" x 5" HT-S graphite fiber 10 plies unidirectional	4" x 4" 181E glass cloth, 12 plies
Processing Conditions	1) R.T. to 390°F in 65 mins./ full vacuum. 2) Hold 390°F for 2 hrs. 3) Heat to 500°F in 25 mins.-apply 100 psi pressure. 4) Heat to 550°F in 10 mins. and cure for 2 hrs.	1) R.T. to 390°F in 65 mins./ full vacuum. 2) Hold 390°F for 3 hrs. 3) Heat to 500°F in 25 mins.-apply 100 psi pressure. 4) Heat to 550°F in 10 mins. and cure for 2 hrs.	Processed same as I-22F-98	1) Kiss pressure at 390°F. 2) Heat to 500°F in 25 mins. apply 200 psi pressure. 3) Heat to 550°F in 10 mins. and cure for 2 hrs.	Processed same as I-22F-104	1) R.T. to 420°F in 70 mins./ full vacuum. 2) Apply 100 psi pressure and heat to 550°F in 50 mins. 3) Cure 2 hrs. at 550°F.
Post Cure	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	550°F/2 hrs.	550°F/2 hrs	575°F/2 hrs.
Resin Content of Laminate	32.2%	26.1%	31.2%	38.1%	40.1%	28.7%
Void Content	4.1%	5.8%	6.6%	--	10.0%	5.1%
500°F Short Beam Shear Strength, MPa	32	34	28	44	44	34
500°F Flexural Strength, MPa	378	347	324	752	561	395
500°F Flexural Modulus, MPa	16,000	--	--	81,600	73,900	16,600

TABLE 2 (Continued)

NADIMIDE TERMINATED SOLUBLE IMIDE PREPOLYMERS - PROCESSING AND PROPERTIES

Laminate No.	I-19N-147	I-229-79	I-229-106	I-229-30	I-229-38
Resin Composition	2 NA/2.5 CPDA/0.5 3,3'MDA/2 BTDA	2 NA/3 DAT/ 2 BTDA	2 NA/3 DAPI/ 2 BTDA	2 NE/3 DAT/ 2 BTDE	2 NE/4 CPDA/ 2 BTDE
Reinforcement	4" x 4" 181E glass cloth, 12 plies	4" x 4" 181E glass cloth, 12 plies	4" x 4" 181E glass cloth, 12 plies	7" x 8" 181E glass cloth, 12 plies	7" x 8" 181E glass cloth, 12 plies
Processing Conditions	1) Heat to 350°F in 1.5 hrs. (no vacuum). 2) Maintain 1 hr. at 350°F. 3) Heat to 460°F in 30 mins. and hold for 1 hr. 4) Apply vacuum and 90 psi pressure. 5) Heat to 550°F in 30 mins. and cure for 2 hrs.	1) Heat to 320°F in 50 mins. at full vacuum. 2) Hold 320°F for 1 hr. 3) Heat to 465°F in 30 mins. and apply 100 psi pressure. 4) Heat to 500°F in 10 mins.-cure for 30 mins. 5) Heat to 550°F in 10 mins. and cure for 1.5 hrs.	1) Heat to 390°F in 65 mins. at full vacuum. 2) Hold 390°F for 2 hrs. 3) Heat to 500°F in 25 mins. and apply 100 psi pressure. 4) Heat to 550°F in 10 mins. and cure for 2 hrs.	1) Heat from R.T. to 370°F in 1 hr. 2) Maintain for 2 hrs. at 370°F 3) Apply 100 psi pressure and raise temperature to 550°F in 40 mins. 4) Cure for 2 hrs. at 550°F.	1) Heat from R.T. to 390°F in 45 mins. 2) Maintain for 2 hrs. at 390°F. 3) Increase temperature to 420°F and apply 90 psi pressure. 4) Increase temperature to 550°F in 50 mins. and cure for 2 hrs.
Post Cure	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.
Resin Content of Laminate	30.7%	31.1%	37.2%	29.4%	32.4%
Void Content	9.0%	10.0%	6.0%	10%	10%
500°F Short Beam Shear Strength, MPa	34	26	31	35	43
500°F Flexural Strength, MPa	360	311	368	346	433
500°F Flexural Modulus, MPa	14,100	14,900	14,700	14,800	15,700

TABLE 3

THERMOGRAVIMETRIC ANALYSES OF POLYIMIDE/'81E

GLASS CLOTH LAMINATES IN NITROGEN ATMOSPHERE*

Laminate No.	Resin Composition	% Resin	% Voids	Weight Loss at 500°C
I-22F-106	2 NA/3 DAPI/2 BTDA	32.2	7.6	8%
I-22F-104	2 NA/3 CPDA/2 BTDA	26.1	5.8	3%
I-22F-87	2 Cinnamal/4 CPDA/ 3 BTDA/2 BMI	30.3	3.2	4%

* Heating rate 5°C/min

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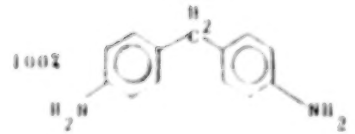
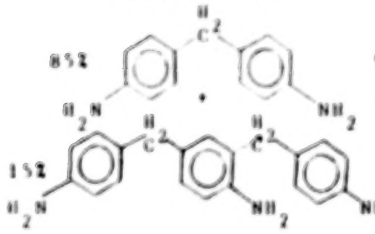
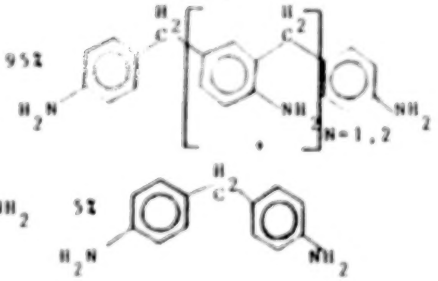
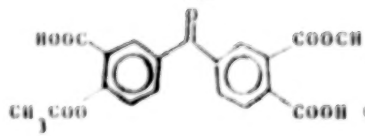
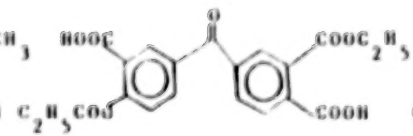
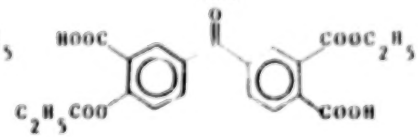
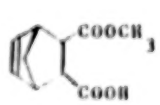
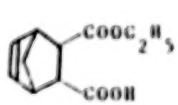
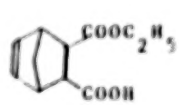
TABLE 4

MONOMERIC REACTANT RESIN FORMULATIONS

Polyimide	PMR-15	LARC-160M	I-25R-151
Aromatic Amine	MDA	Jeffamine AP-22[1]	BABA[2]
Amine Composition	100% 	85%  15%	95%  N=1,2 5%
Amine Equivalent, gms	99	102	105
Calculated Molecular Weight	198	234	315
BTDE-Aromatic Dianhydride[3] Precursor			
NE-Nadic Anhydride[4] Precursor			
Monomeric Molar Ratios NE/Amine/BTDE	1.00/1.50/1.00	1.82/1.61/1.00	1.84/1.23/1.00
Melt Prepregging Capability	no	yes	yes

(1) Jefferson Chemical
(2) DuPont
(3) Gulf Development
(4) Eastman Kodak

TABLE 5

NA/BABA/BTDA IMIDE PREPOLYMERS

NA/BABA/BTDA Molar Compositions	Melting Range °C
3.0/1.00/zero	180
4.00/2.00/1.00	195-206
3.50/1.83/1.00	198-212
3.00/1.66/1.00	216-234
2.50/1.50/1.00	225-243
2.00/1.33/1.00	228-252
1.85/1.23/1.00	235-260
1.50/1.16/1.00	incomplete melting
NA/PA*/BABA/BTDA Molar Compositions	
1.85/0.65/1.50/1.00	240-249
1.00/1.50/1.50/1.00	213-227

*Phthalic anhydride

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TABLE 6

VACUUM BAG-AUTOCLAVE PROCESSING OF BABA BASED POLYIMIDE/HT-S GRAPHITE FIBER LAMINATES

Laminate No.	I-25R-40	I-25R-41	I-25R-43	I-25R-44	I-25R-54
No. of Plies	12	11	11	11	12
Size of Plies	4" x 4"	4" x 4"	4" x 4"	4" x 4"	6" x 6"
Processing Conditions	1) Heat to 400°F under 2" vacuum. 2) Maintain 400°F/ 2" vacuum for 1 hrs. 3) Heat to 490°F and apply 200 psi pressure. 4) Heat to 550°F and cure 1 hr.	1) Heat to 194°F. under 2" vacuum and maintain for 1 hr. 2) Heat to 400°F and maintain for 3 hrs. 3) Heat to 490°F and apply 200 psi pressure. 4) Heat to 550°F and cure 1 hr.	1) Heat to 400°F. in 1 hr. with no vacuum. 2) Apply 2" vacuum at 400°F and maintain 3 hrs. 3) Heat to 490°F and apply 200 psi pressure. 4) Heat to 550°F and cure 1 hr.	1) Heat to 194°F with no vacuum. 2) Maintain 194°F for 1 hr. and then apply 2" vacuum. 3) Heat to 400°F and maintain for 3 hrs. 4) Heat to 490°F and apply 200 psi pressure. 5) Heat to 550°F and cure 1 hr.	Same processing conditions as run no. I-25R-44
Resin Flow	35%	59%	6.4%	38%	15%
Resin Content of Laminate	30.5%	25.0%	41.2%	33%	33%
Fiber Volume	--	--	--	60.5%	60.5%
500°F. SBS Strength, MPa*	36	36	46	54	46
500°F. Flexural Strength, MPa*	--	--	--	1,040	1,000
500°F. Flexural Modulus, MPa*	--	--	--	124,000	119,000

* Laminate strength properties taken after 600°F/2 hour post cure.

TABLE 7

VACUUM BAG-AUTOCLAVE PROCESSING OF BABA BASED POLYIMIDE/CELION 6000 GRAPHITE FIBER LAMINATES

Laminate No.	I-25R-150	I-25R-151	I-25R-152	I-27D-1	I-27D-2	I-27D-3
NA/F/BTDA Ratio	2.5/1.50/1.00	1.85/1.23/1.00	2.0/1.33/1.00	4.0/2.00/1.00	3.5/1.83/1.00	3.0/1.66/1.00
Melting Range of Imide Prepolymer	225-243°C	235-265°C	228-252°C	195-206°C	198-212°C	216-234°C
No. of Plies	24	24	23	23	24	24
Laminate Dimensions	6" x 6" x 1/8"	6" x 6" x 1/8"	6" x 6" x 1/8"	6" x 6" x 1/8"	6" x 6" x 1/8"	6" x 6" x 1/8"
Vacuum Bag-Autoclave Processing Procedure	II	II	II	II	II	II
Resin Flow	75.0%	74.0%	72.8%	77.0%	74.0%	75.0%
Resin Content	26.3%	29.1%	31.0%	25.7%	27.0%	25.2%
Fiber Volume	67.8%	64.9%	62.7%	63.8%	67.2%	68.4%
Laminate Density	1.62	1.61	1.60	1.63	1.62	1.62
Void Content	0	0	0	0	0	0
500°F. Short Beam Shear Strength, MPa(1)	57	61	52	--	--	--
600°F. Short Beam Shear Strength, MPa(1)	52	47	45	52	52	53
Room Temperature Short Beam Shear Strength, MPa(1)	--	87	--	--	--	--

(1) After a 600°F/2 hour post cure.

TABLE 8

VACUUM BAG-AUTOCLAVE PROCESSING PROCEDURES FOR BABA BASED POLYIMIDES

I

1. Heat to 194°F./25 minutes - maintain 194°F./1 hour
2. Apply 2" vacuum - heat to 400°F./40 minutes
3. Maintain 400°F./2" vacuum/3 hours
4. Heat to 490°F./20 minutes - apply 200 psi pressure
5. Heat to 550°F./5 minutes - maintain 550°F./200 psi/1 hour

II

1. Heat to 194°F./25 minutes - maintain 194°F./1 hour
2. Apply 2" vacuum - heat to 325°F./30 minutes
3. Maintain 325°F./2" vacuum/3 hours
4. Heat to 525°F./40 minutes - apply 200 psi pressure
5. Heat to 550°F./5 minutes - maintain 550°F./200 psi/1 hour

III

1. Heat to 194°F/25 minutes - maintain 194°F/1 hour
2. Apply 2" vacuum - heat to 375°F/36 minutes
3. Apply full vacuum and maintain 375°F/2 hou
4. Heat to 540°F/33 minutes - apply 200 psi pressure
5. Heat to 550°F/5 minutes - maintain 550°F/200 psi/1 hour

TABLE 9

ECONOMICS OF BABA BASED POLYIMIDES

Polyimide 1.85 NA/1.23 BABA/1.00 BTDA

Monomer	Wt. %	Estimated Cost/lb.	Total Cost
BTDA	31.8	2.30	0.73
NA	29.8	1.00	0.30
BABA	38.4	0.30	0.11
		TOTAL MATERIAL COST	$1.14/lb.

PA Polyimide 1.00 NA/1.5 PA/1.5 BABA/1.00 BTDA

Monomer	Wt. %	Estimated Cost/lb.	Total Cost
BTDA	27.8	2.30	0.64
NA	14.1	1.00	0.14
PA*	19.1	0.30	0.06
BABA	39.0	0.30	0.12
		TOTAL MATERIAL COST	$0.96/lb.

* Phthalic anhydride

TABLE 10

PREPARATION OF 9.65 KILOGRAMS OF BABA BASED POLYIMIDE RESIN

Run No.	I-26J-139-20, 144-25, 148-24		
Monomer Ratio	1.85/1.23/1.00		
BTDA Purification	Acetone extracted 30 minutes and dried @ 130°C./24 hours		
BTDA Assay	Theory	161.3 g/eq	
	Found	165.8 g/eq	
Anhydride Charge	BTDA	2581	(16.00 eq)
	NA	2421	(14.75 eq)
	Ethanol	1564	(34.00 eq - 10.6% excess)
Reaction Conditions	80-85°C./4 hours - anhydrous		
Ester Product			
Yield	6552 g (99.8%)		
Acid Assay[1]			
Theory	214 g/eq		
Found	214 g/eq (initial value and after five weeks storage)		
BABA Charge[2]	3099 g (29.5/eq)		
Total Resin Weight	9651 g		

---

[1] Ester product contains 2.29% by weight etharol.

[2] BABA (96% of ester eq.) and ester product were used at 35% by weight in acetone for prepregging.

TABLE II

BABA BASED POLYIMIDE/UNIDIRECTIONAL

CELION 6000 GRAPHITE FIBER LAMINATE I-27U-43

NA/BABA/BTDA Ratio	1.85/1.23/1.00
No. of Plies	19
Laminate Dimension	7" x 7" x 1/8"
Vacuum Bag-Autoclave Procedure	III
% Resin Flow	29%
% Resin Content	32.9%
Vf	59.1%
Void Content	2%
Post Cure	600°F/2 hours
Short Beam Shear Strength, MPa	
@ 75°F	93
@ 500°F	57
@ 600°F	46
Flexural Strength, MPa	
@ 600°F	807
Flexural Modulus, MPa	
@ 600°F	104,000

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TABLE 12

VACUUM BAG-AUTOCLAVE PROCESSING OF MONOETHYL PHTHALATE FORMULATED BABA BASED POLYIMIDES

Laminate No.	I-27U-7	I-27U-9	I-27U-10
NA/PA/BABA/ BTDA Ratio	1.84/0.66/1.5/1.00	1.85/0.66/1.5/1.00	1.67/0.33/1.33/1.00
Melting Range of Imide Prepolymer	213 - 221°C	213 - 227°C	--
No. of Plies	23	24	24
Laminate Dimensions	3" x 4" x 1/8"	6" x 6" x 1/8"	6" x 6" x 1/8"
Vacuum Bag-Autoclave Processing Procedure	II	II	II
Resin Flow	72.0%	74.5%	71.0%
Post Cure	600°F/2 hours	600°F/2 hours	600°F/2 hours
Resin Content	28.0%	28.2%	32.0%
Fiber Volume	65.0%	65.7%	61.4%
Laminate Density	1.59	1.61	1.59
Void Content	1.3%	0	0
600°F. Short Beam Shear Strength, MPa	35	32	35
Room Temperature Short Beam Shear Strength, MPa	99	--	89

TABLE 13

PROCESSING AND PROPERTIES OF A-2 ALTERNATE POLYIMIDE I-19N-124

Laminating Varnish	30% resin in 50/50 dioxane/ethylene dichloride
Prepreg	181E glass cloth
Plies	13 (8" x 8")
Vacuum Bag-Autoclave Processing Conditions	(1) R.T. to 221°F in 45 minutes. (2) Maintain 221°F for one hour. (3) Heat to 338°F in 45 minutes and apply 100 psi pressure. (4) Heat to 400°F in 30 minutes and cure for two hours.
Post Cure Conditions	Heat from R.T. to 575°F in 18 hours - Maintain 575°F for two hours
Resin Content	33.6%
Void Content	0%
Flexural Strength, MPa	
R.T.	441
500°F	435
550°F	425
Flexural Modulus, MPa	
R.T.	17,600
500°F	16,400
550°F	15,400
Short Beam Shear Strength, MPa	
R.T.	37
500°F	36
Smoke Density Test	
Non-Flaming Dm	7.0
Time to 90% Dm in Minutes	15.3
Flaming Dm	42
Time to 90% Dm in Minutes	11.9
D_s = 16	6.2
TMA, Heat Distortion Temperature	775°F

TABLE 14

THERMOMECHANICAL ANALYSIS OF A-2 ALTERNATE

POLYIMIDE/181E GLASS LAMINATE I-19N-124

Post Cure Temperature °F	TMA Penetrometer "Heat Distortion Point" °F
500	669
550	743
575	765
600	775

TABLE 15

TORSIONAL BRAID CURING STUDY ON A-2 ALTERNATE POLYIMIDE I-19N-145B

Curing Temperature °C	Curing Time, Minutes	Tg
204	90	230°C
250	30	285°C
300	155	310°C

TABLE 16

PROCESSING AND PHYSICAL PROPERTIES OF 2 CINNAMAL/3 CPDA/2 BTDA/1.5 BMI

POLYIMIDE RESIN I-19N-145B

Resin Solids Content	29%
Void Content	1.2%
500°F Flexural Strength, MPa	373
500°F Flexural Modulus, MPa	16,700
500°F Short Beam Shear Strength, MPa	44
Thermomechanical Analyzer Penetrometer "Heat Distortion Point" °F	621

TABLE 17

2 CINNAMAL/4 CPDA/3 BTDA/2 BMI A-2 ALTERNATE POLYIMIDES

Laminate No.	I-22F-71	I-22F-80	I-22F-84	I-22F-87	I-22F-96[2]	I-22F-90[2]
Processing[1] Conditions	vacuum bag-autoclaving 1) R.T. to 338°F in 1 hr. under full vacuum. 2) Apply 100 psi pressure and hold at 338°F/1 hr. 3) Heat to 400°F in 15 mins. 4) Cure 2 hrs. @ 400°F.	press lamination 1) B-stage prepreg in oven at 221°F/1 hr. 2) Press @ 400°F/200 psi/1.5 hrs.	press lamination 1) B-stage prepreg in oven at 221°F/1 hr. 2) Press @ 400°F/200 psi/2.0 hrs.	press lamination 1) B-stage prepreg in oven at 194°F/1 hr. 2) Press @ 410°F/200 psi/2.0 hrs.	vacuum bag-autoclaving 1) R.T. to 320°F in 1 hr. under full vacuum 2) Apply 100 psi pressure and hold @ 338°F for 1 hr. 3) Heat to 400°F in 15 mins. 4) Cure 2 hrs. @ 400°F	vacuum bag-autoclaving 1) R.T. to 338°F in 1 hr. under full vacuum. 2) Apply 100 psi and hold @ 338°F for 1 hr. 3) Heat to 400°F in 15 mins. 4) Cure 2 hrs. @ 400°F.
Post Cure	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.
Resin Content of Laminate	32.6%	25.4%	32.4%	30.3%	33.8%	37.5%
Void Content	1.5%	zero	1%	3%	3.9%	zero
500°F Flexural Strength, MPa	449	565	469	447	329	424
500°F Flexural Modulus, MPa	--	21,000	18,900	18,700	14,500	--
500°F Short Beam Shear Strength, MPa	35	48	49	48	32	38
After 500°F Oxidative Aging						
250 Hours	--	--	--	--	--	19
500 Hours	--	--	--	--	--	16
750 Hours	--	--	--	--	--	15

(1) 181E glass cloth laminates
(2) Three moles of BMI per mole of imide prepolymer.

TABLE 18

A-2 ALTERNATE POLYIMIDE/181E GLASS LAMINATES PREPARED FROM VARIOUS DIAMINES[1]

Laminate No.	I-22F-27	I-22F-29	I-19N-124
Diamine	DAT	3,3'MDA	CPDA
Resin Content - Weight %	29.7	34.0	33.6
Void Content by Density	8%	--	0%
Flexural Strength at 500°F, MPa	313	laminate heat distorted	435
Flexural Modulus at 500°F, MPa	15,400	laminate heat distorted	16,400
Short Beam Shear Strength at 500°F, MPa	36	laminate heat distorted	36

(1) All resins were processed from 50/50 dioxane/ethylene dichloride laminating varnishes by the 400°F vacuum bag-autoclave procedure shown in Table 13.

TABLE 19

TBA CURING STUDIES ON 400°F AUTOCLAVABLE POLYIMIDES

Batch No.	End Capping Group	MW	Curing Temperature °C	Tg °C
I-19Y-66A[1]	cinnamal	1228	204	240
			300	365
I-19Y-33[2]	amino	939	204	235
			300	380
I-19Y-138[3]	amino	1347	204	230
			300	330

(1) 2 cinnamal/3 CPDA/2 BTDA/2 BMI A-2 Alternate Resin

(2) 3 DAT/2 BTDA/2 BMI A-2 Resin

(3) 4 DAT/3 BTDA/2 BMI A-2 Resin

TABLE 20

400°F VACUUM BAG-AUTOCLAVE PROCESSING OF A-2 RESIN 3 DAT/2 BTDA/2 BMI

Run No.	I-19N-148	I-22F-14
Laminate Dimensions	4" x 4" x 1/8"	7" x 8" x 1/8"
Vacuum Bag-Autoclave Processing Conditions	1) Heat from room temperature to 311°F in 75 minutes under full vacuum. 2) Maintain for 3 hours at 311°F under full vacuum. 3) Apply 90 psi pressure and then raise temperature to 400°F in 35 minutes. 4) Maintain at 400°F/90 psi/full vacuum for 2 hours.	
Resin Melt Flow	0.1%	2.5%
Post Cure Conditions	575°F/2 hours	575°F/2 hours*
Resin Solids Content	28.4%	30.9%
Void Content	6.8%	4.9%
500°F Flexural Strength, MPa	424	401
500°F Flexural Modulus, MPa	17,800	16,300
500°F Short Beam Shear Strength, MPa	37	39

* Laminate blistered upon post curing at 525°F.

TABLE 21

400°F VACUUM BAG-AUTOCLAVE PROCESSING OF A-2 RESIN 4 CPDA/3 BTDA/2 BMI

Run No.	I-22F-102	I-22F-33	I-22F-36	I-22F-41
Prepreg B-Staging Conditions	1 hr. @ 374°F	30 mins. @ 248°F	30 mins. @ 248°F	30 min. @ 248°F
Vacuum Bag-Autoclave Processing Conditions	1) R.T. to 311°F in 60 mins. 2) Maintain 311°F for 1 hr. 3) Apply 100 psi pressure and heat to 400°F in 25 mins. 4) Cure for 2 hrs. at 400°F.	1) R.T. to 302°F in 75 mins. 2) Maintain 302°F for 3 hrs. 3) Apply 100 psi pressure and heat to 400°F in 35 mins. 4) Cure for 2 hrs. at 400°F.	1) R.T. to 257°F in 50 mins. 2) Maintain 257°F for 3 hrs. 3) Apply 100 psi pressure and heat to 400°F in 45 mins. 4) Cure for 2 hrs. at 400°F.	1) R.T. to 257°F in 50 mins. 2) Maintain 257°F for 1 hr. 3) Apply 100 psi pressure and heat to 400°F in 45 mins. 4) Cure 2 hrs. at 400°F.
Post Cure	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.	575°F/2 hrs.
% Resin Melt Flow	2	5.4	3.0	6.3
% Resin Content	29	33	32	32
% Void Content	11	+10	10	9.1
500°F Flexural Strength, MPa	376	233	415	411
500°F Flexural Modulus, MPa	16,200	12,300	16,100	15,900
500°F Short Beam Shear Strength MPa	27	17	30	30

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TABLE 22

NCNS-12M/HT-S UNIDIRECTIONAL GRAPHITE FIBER LAMINATE

I-19N-120

Laminating Varnish	50% by wt. in methanol/ethylacetate 60/40
Plies	Twelve 9 3/4" x 9 3/4"
B-Stage	1 hour-70°C-draft oven, 15 minutes-90°C-vacuum oven
Press Laminating Conditions	350°F/1.5 hours-400°F/1 hour-600 psi
Postcure	450°F/5 hours
Resin Content	41%
Fiber Volume V/O	52.8
% Void Content by Density	>1

TABLE 23

OXIDATIVE AGING OF NCNS-12M/HT-S GRAPHITE

LAMINATE I-19N-120

	77°	400°F	Retention of 400°F Strength
Short Beam Shear Strength, MPa	81	57	--
250 Hours	112	35	62%
500 Hours	110	50	87%
750 Hours	116	50	88%
1000 Hours	118	36	63%
1250 Hours	116	61	106%
1500 Hours	117	49	87%

TABLE 24

WATER BOIL TESTS ON NCNS-12M/HT-S GRAPHITE

FIBER LAMINATE I-19N-120

	77°F	Retention	350°F	Retention
Initial SBS Strength, MPa	81	--	61	--
SBS Strength after 24 Hours H_2O Boil, MPa	101	125%	52	85%
SBS Strength after 24 Hours H_2O Boil and drying under Vacuum at 110°C, MPa	--	--	53	87%

TABLE 25

HUMIDITY AGING DATA ON NCNS-12M/HT-S

UNIDIRECTIONAL GRAPHITE FIBER LAMINATES

Laminate No.	I-22F-22A	I-22F-145	I-24A-79
No. of Plies	11	12	10
Graphite Fiber	HT-S	AS	HT-S
Press Molding Conditions	400°F/600 psi/ 1.5 hr	350-400°F/600 psi/ 1.5 hr	350-400°F/600 psi/ 2.0 hr
Post Cure Conditions	450°F/4 hr	450°F/4 hr	400°F/22 hours
Resin Content	39.3%	39.2%	34.1%
Fiber Volume, Vf	55.0%	53.7%	61.0%
Initial 350°F Short Beam Shear Strength, MPa	82	77	66
After 30 Day, 95% R.H., 120°F Exposure, MPa	35	34	45 (55)*
% Retention of 350°F Short Beam Shear Strength	42	44	68
% Water Absorbed in 30 Days	--	--	1.13

* Half of the laminate given the 400°F/22 hour post cure was given an additional 22 hour post cure at 450°F and humidity aged to yield this higher strength.

TABLE 26

VACUUM BAG-AUTOCLAVE PROCESSING OF NCNS-12M RESIN

Laminate No.	I-22F-37	I-24A-80
Reinforcement	181E glass cloth	HT-S graphite fiber
Processing Conditions	1) R.T./vacuum/1 hr 2) Heat to 158°F in 17 min and hold @ 158°F for 90 mins /vacuum. 3) Heat to 194°F in 10 min and hold 194°F for 15 min /vacuum. 4) Apply 100 psi pressure and heat to 400°F in 40 min /vacuum. 5) Cure @ 400°F for 1 hr /vacuum.	1) R.T./vacuum/1 hr 2) Heat to 158°F in 17 min and hold @ 158°F for 3 hr /vacuum. 3) Heat to 194°F in 10 min and hold 194°F for 15 min /vacuum. 4) Apply 100 psi pressure and heat to 350°F in 40 min /vacuum. 5) Cure @ 350°F for 2 hr /vacuum.
% Resin Flow	5	4
Post Cure Conditions	450°F/2 hr	450°F/19 hr
% Resin Content	31.2	33.1
% Fiber Volume, Vf	--	62
% Void Content	None	0.2
Flexural Strength, MPa		
R.T.	444	--
400°F	374	--
Flexural Modulus, MPa		
R.T.	22,100	--
400°F	18,000	--
Short Beam Shear Strength, MPa		
R.T.	60	--
400°F	46	61

TABLE 27

DELSEN CORPORATION SMOKE AND FLAMMABILITY

TEST DATA ON NCNS-12M LAMINATES

Laminate No.	I-19N-13A	I-19N-18
Reinforcement	Kevlar 49, Type 3 fabric	181E glass fabric
B-Staging Conditions	30 min @ 90°C, 15 min @ 120°C	30 min @ 90°C, 15 min @ 120°C
Press Laminating Conditions	350°F/1.5 hr -400°F/ 1 hr /800 psi	350°F/2 hr /600 psi
Post Cure Conditions	450°F/5 hr	450°F/4 hr
Resin Content	51.0%	34.4%
Fiber Volume	46.7%	50.1%
Void Content	2.4%	2.3%
ASTM D2843-70 Smoke Rating Density @ 4 min	39%	32%
Federal Aviation 60 seconds Vertical Burn Test 25.853A		
Flame Time	11 seconds	12 seconds
Burn Length	1.5 inches	1.3 inches
Flame Time of Dripping	non-dripping	non-dripping

TABLE 28

AMERICAN INSTRUMENT COMPANY SMOKE DENSITY DATA

	NCNS-12M Laminate	P13N Laminate
Resin Content	29.9%	27.0%
Fiber Volume	54.8%	--
Void Content	0%	0%
Maximum Specific Optical Density (Dm)		
Flaming	20	20
Non-Flaming	6	0.3
Time in Minutes to Develop Specific Optical Density, D_s = 16		
Flaming	6.6	7.5
Non-Flaming	not reached	not reached
Oxygen Index of Neat Resin	29	31
Oxygen Index of Laminates	86	--

TABLE 29

COMPARISON OF 181E GLASS, KEVLAR 49, AND HT-S GRAPHITE LAMINATES IN AMERICAN INSTRUMENT COMPANY SMOKE DENSITY CHAMBER

Laminate	NCNS-12M/181E Glass	NCNS-12M/Kevlar	NCNS-12M/HT-S Graphite
% Resin Content	30	31	41
Maximum Specific Optical Density (Dm) Under Flaming Conditions	20	88	107
Time in Minutes to Develop Specific Optical Density (D_s = 16)	6.6	1.9	2.8
Time in Minutes to Develop (D_s = 100)	not reached	not reached	6.5

TABLE 30

PHYSICAL PROPERTIES OF UNFILLED

MOLDED 1/8" PLAQUE OF NCNS-12M RESIN

Run No.	I-24A-81
Density	1.34
Barcol Hardness	52-53
Heat Distortion Temperature	250°C.
Flex. Str., R.T., MPa	108
Flex. Str., 400°F., MPa	99.4
Flex. Mod., R.T., MPa	4,150
Flex. Mod., 400°F., MPa	3,020
Tensile Str., R.T., MPa	62.1
Tensile Str., 400°F., MPa	61.4
Tensile Mod., R.T., MPa	3,880
% Elongation, R.T.	1.6
Water Absorption, 24 hours Immersion at R.T.	0.67%
Limiting Oxygen Index	29

TABLE 31

POST CURE STUDY ON NCNS-12M/181E GLASS

LAMINATE I-19N-125

Temperature °F	no post cure	400	425
Time in Hours	zero	14	14
Flexural Strength, MPa			
R.T.	462	464	465
400°F	323	355	365
Flexural Modulus, MPa			
R.T.	22,800	22,700	23,000
400°F	19,200	20,400	20,100
Short Beam Shear Strength, MPa			
R.T.	55	54	54
400°F	25	27	32
TMA Penetrometer "Heat Distortion" °C	248	257	258

TABLE 32

THERMOMECHANICAL ANALYSIS OF POST CURES ON

NCNS-12M/181E GLASS LAMINATES

Post Cure Temperature °F	TMA Penetrometer "Heat Distortion Point" °F
No postcure	487
400	498
425	509
440	550
450	561
460	545

TABLE 33

181E GLASS LAMINATE PREPARED

FROM NCNS-12M RESIN STORED AT ROOM TEMPERATURE FOR ONE YEAR

% Resin Content	27.2
% Void Content	0.8%
400°F Flexural Strength, MPa	483
400°F Flexural Modulus, MPa	19,900
400°F Short Beam Shear Strength, MPa	31

TABLE 34

ROOM TEMPERATURE STORAGE STABILITY OF NCNS-12M

LAMINATING VARNISH OF 50% RESIN SOLIDS CONCENTRATION

Laminate No.	I-24A-3	I-24A-14
Reinforcement	181E glass fabric	181E glass fabric
Laminating Varnish Storage Period in Days	1	30
Prepreg Drying Conditions	158°F/1 hr	158°F/1 hr
Prepreg B-Staging Conditions	230°F/15 min	302°F/15 min
Press Laminating Conditions	350°F/1.5 hr 400°F/1 hr -600 psi	350°F/1.5 hr 400°F/1 hr -600 psi
Post Cure Conditions	435°F/5 hr	435°F/5 hr
% Resin Content of Laminate	29.8	39.1
400°F Flexural Strength, MPa	391	391
400°F Flexural Modulus, MPa	19,500	17,300
400°F SBS Strength, MPa	41	44

TABLE 35

NCNS-12M/181E GLASS PREPREG STORAGE STABILITY*

Run No.	I-22F-132	I-22F-132-A	I-24A-11	I-24A-25
Storage Period in Days	1	30	30	60
Condition	wet, tacky	dry, boardy	wet, tacky	wet, tacky
B-Staged	194°F/15 min	194°F/15 min	239°F/15 min	248°F/15 min
Resin Content	29.4%	30.8%	30.7%	30.4%
400°F. Flex. Strength, MPa	480	383	455	375
400°F. Flex. Modulus, MPa	21,000	20,300	19,600	18,100
400°F. SBS Strength, MPa	44	41	37	35

* Laminate properties were determined after a 450°F post cure.

TABLE 36

RAPID PRESS LAMINATING PROCESSES FOR NCNS-12M RESIN

Run No.	I-24A-8	I-24A-12	I-24A-19	I-24A-28
Laminating Varnish	50% resin in 60/40 methanol/ethylacetate	50% resin in 60/40 methanol/ethylacetate	35% resin in 90/10 methylene chloride/ methanol	35% resin in 90/10 methylene chloride/ methanol
B-Staging Conditions	prepreg heated @ 100°C/15 min.	prepreg heated @ 90°C/15 min.	resin heated @ 85°C/30 min. before dissolving	resin heated @ 85°C/30 min. before dissolving
Press Laminating Cycle*	slow control	rapid processing	slow control	rapid processing
Press Laminating Conditions	350°F/1.5 hrs. 400°F/1 hr. @ 600 psi	350°F/3 min. @ 200 psi	350°F/1.5 hrs. 400°F/1 hr. @ 200 psi	350°F/5 min. @ 200 psi
Post Cure Conditions	R.T. to 435°F in 18 hrs.-held at 435°F for 5 hrs.	350°F to 435°F in 20 min.-held at 435°F for 2 hrs.	R.T. to 435°F in 18 hrs.-held at 435°F for 5 hrs.	350°F to 435°F in 20 min.-held at 435°F for 2 hrs.
Resin Content	31.1%	31.7%	31.9%	32.2%
400°F Flexural Strength, MPa	426	446	489	469
400°F Flexural Modulus, MPa	20,400	20,300	21,900	20,000
400°F SBS Strength, MPa	43	35	56	54

* Each run press laminated 14 plies of 181E glass fabric prepreg that had been oven dried for 1 hour at 70°C. Glass fabric was Clark-Schwebel style 1581, A-1100 size-hard finish.

TABLE 37

HUMIDITY AGING OF XYLYLENEDIAMINE BASED AND JEFFAMINE AP-22 BASED NCNS RESIN/GRAPHITE FIBER LAMINATES

Laminate No.	I-24A-9A	I-24A-15A
NCNS Resin Composition	NCNS-12X	NCNS-12J
Graphite Fiber	Hercules HT-S	Hercules HT-S
No. of Plies	12	12
Drying Conditions	70°C/1 hr	70°C/1 hr
B-Staging Conditions	120°C/15 min	90°C/15 min
Press Laminating Conditions	435°F/600 psi/2.5 hr	435°F/600 psi/2.5 hr
Post Cure Conditions	435°F/4 hr	450°F/4 hr
Resin Content	40.2%	37.2%
Fiber Volume	52.2%	56.6%
Initial 350°F SBS Strength, MPa	68	58
350°F SBS Strength after Humidity Aging, MPa	29	44
350°F SBS Strength after 24 Hours Water Boil, MPa	52	55

TABLE 38

NCNS-13P/181E GLASS CLOTH LAMINATES

Laminate No.	I-24A-58	I-25R-26	I-25R-58
Laminating Varnish	70/30 THF/ ethyl acetate	80/20 methylene chloride/methanol	methylethyl ketone
No. of Plies	14	14	15
Prepreg Drying Conditions	70°C/1 hr	70°C/1 hr	70°C/1 hr
B-Staging Conditions	90°C/15 min	110°C/30 min	120°C/30 min
Press Laminating Conditions	350°F/600 psi/5 min	350°F/600 psi/1 hr	350°F/600 psi/1 hr
Post Cure	450°F/4 hr	425°F/7 hr - 460°F/8 hr	425°F/7 hr - 460°F/8 hr
Resin Content	32.0%	24.6%	24.3%
400°F Flexural Strength, MPa	380	595	--
400°F Flexural Modulus, MPa	19,300	25,500	--
400°F Short Beam Shear Strength, MPa	48	69	71

TABLE 39

NCNS-12P RESIN/HT-S UNIDIRECTIONAL

HT-S GRAPHITE FIBER LAMINATES

Laminate No.	I-24A-50	I-24A-50A
Prepreg Drying Conditions	70°C/1 hr	70°C/1 hr
B-Staging Conditions	110°C/15 min	120°C/15 min
Press Laminating Conditions	350°F/1.5 hr -400°F/ 1 hr., 600 psi	350°F/1.5 hr -400°F/ 1 hr., 600 psi
Post Cure	460°F/4 hr	460°F/60 hr
Resin Solids Content	27.1%	31.1%
Fiber Volume	66.1%	62.9%
Void Content	1%	0
350°F Short Beam Shear Strength, MPa	87	83
350°F SBS Strength after 24 Hours Water Boil, MPa	68	66
350°F SBS Strength after 96 Hours Water Boil, MPa	62 (72 hr) 46	49
Water Absorption after 24 Hours Water Boil	0.63%	0.56%
Water Absorption after 96 Hours Water Boil	0.98%	0.70%
Thermal Mechanical Analysis-Temperature of Rapid Expansion of Z axis	248°C	278°C

TABLE 40

EFFECT OF BOILING WATER ON NCNS/UNIDIRECTIONAL HT-S GRAPHITE FIBER LAMINATES

Laminate No.	I-22F-145	I-24A-15	I-24A-50
NCNS Resin	NCNS-12M	NCNS-12J	NCNS-12P
Resin Content	39.2%	36.9%	27.2%
Fiber Volume	53.7%	57.2%	66.1%
350°F Short Beam Shear Strength Before Water Boil, MPa	70	79	87
350°F Short Beam Shear Strength after 24 Hour Water Boil, MPa	46	55	68
Water Absorption After 24 Hours Boil	--	1.06%	0.63%
Water Absorption After 96 Hours Boil	--	1.23%	0.98%

TABLE 41

WATER ABSORPTION OF NCNS-13P/HT-S GRAPHITE FIBER LAMINATES

Laminate No.	I-24A-76B	I-24A-105	I-24A-105A
No. of Plies	12	10	14
Post Cure	450°F/19 hr (one stage)	400°F/10 hr - 450°F/10 hr	400°F/10 hr - 450°F/10 hr
% Water Absorbed			
After 7 Days	0.86	0.86	0.74
14 Days	1.11	1.11	0.97
21 Days	1.36	1.30	1.18
28 Days	1.42	1.33	1.27

TABLE 42

HUMIDITY AGING STUDIES ON NCNS-HT-S GRAPHITE FIBER LAMINATES AND COMPETITIVE LAMINATES

Laminate No.	I-24A-50	I-24A-50A	I-24A-64A	I-24A-105	I-24A-82	I-24A-97
Resin	NCNS-12P	NCNS-12P	NCNS-13P	NCNS-13P	Narmco 5208*	Hexcel F-178*
Post Cure Conditions	460°F/4 hrs.	460°F/60 hrs.	460°F/4 hrs.	400°F/10 hrs.-450°F/10 hrs.	400°F/4 hrs.	400°F/4 hrs.-475°F/10 hrs.
Resin Solids Content	27.1%	31.3%	42.6%	30.1%	30.0%	32.0%
Fiber Volume	66.1%	62.9%	51.4%	63.1%	65.0%	65.0%
Initial 350°F Short Beam Shear Strength, MPa	87	83	75	78	59	68
350°F Short Beam Shear Strength after 24 Hours Water Boil, MPa	68	66	66	--	57	--
350°F Short Beam Shear Strength after 96 Hours Water Boil	46	49	55	--	41	--
350°F Short Beam Shear Strength after 30 Day, 120°F, 95% R.H., MPa	44	47	48	53 68 (300°F)	37	33
% Water Absorption after 96 Hours Water Boil	0.98%	0.70%	0.83%	--	--	--
Tg by TMA	248°C	278°C	286°C	--	--	--

* These Thornel 300 based prepregs were purchased from the respective companies.

TABLE 43

VACUUM BAG-AUTOCLAVE PROCESSING OF NCNS-13P RESIN/AS GRAPHITE FIBER LAMINATES

Laminate No.	1-24A-133	1-270-11	1-270-21	1-270-22	1-270-28
Laminating Varnish	32% resin in 60/40 methanol/ethylacetate	30% resin in acetone	30% resin in acetone	30% resin in acetone	30% resin in MEK
Vacuum Bag-Autoclave Processing Conditions	1) Heat to 212°F in 25 min./vacuum. 2) Hold 212°F for 30 min. 3) Heat to 257°F in 9 min. and apply 100 psi pressure. 4) Heat to 400°F in 30 min. and cure 1 hr.	1) Heat to 212°F in 25 min./vacuum. 2) Hold 212°F for 30 min. 3) Heat to 257°F in 9 min. and apply 100 psi pressure. 4) Heat to 400°F in 32 min. and cure 1 hr.	1) Vacuum/R.T./1 hr. 2) Heat to 140°F in 12 min.-hold at 140°F for 1 hr. 3) Heat to 239°F in 20 min. and apply 100 psi pressure. 4) Heat to 400°F in 32 min. and cure 1 hr.	1) Vacuum/R.T./1 hr. 2) Heat to 140°F in 12 min.-hold at 140°F for 1 hr. 3) Heat to 239°F in 20 min. and apply 100 psi pressure. 4) Heat to 400°F in 32 min. and cure 15 min.	1) Vacuum/R.T./1 hr. 2) Heat to 140°F in 12 min.-hold at 140°F for 1 hr. 3) Heat to 239°F in 20 min. and apply 100 psi pressure. 4) Heat to 400°F in 32 min. and cure 1 hr.
% Resin Flow	4.0	3.7	6.0	3.0	2.1
% Resin Content	36.9	34.9	33.5	35.2	36.2
Vf	60.0	57.2	58.5	57.0	56.0
Density	1.57	1.58	1.60	1.59	1.60
% Voids	zero	1.2%	1.0%	0.6%	0.2%
400°F. SBS Strength, MPa*	61 (69 @ 350°F)	57	86	78	67

* After 425°F/7 hr.-460°F./8 hr. post cure.

TABLE 44

NCNS-13P RESIN PILOT PLANT BATCH NO. 7/7/1002

Melting Point	107-116°C
Gelation Time @ 125°C	8 minutes
Elemental Analysis	%C 67.9; %H 4.63; %N 17.4; %S 4.85
Laminating Varnish I-25R-99	30% NCNS-13P in 60/40 methanol/ethyl acetate
Reinforcement	unidirectional AS graphite fiber
B-Staging Conditions for Prepreg	70°C/75 min - 85°C/15 min
No. of Plies	15
Press Laminating Conditions	325°F/300 psi/1 hr
Post Cure Conditions	425°F/7 hr - 460°F/8 hr
Resin Solids Content	30.3%
Fiber Volume	64.8%
Void Content	none
400°F Short Beam Shear Strength, MPa	79
400°F Flexural Strength, MPa	1,640
400°F Flexural Modulus, MPa	119,000

TABLE 45

FAA VERTICAL BURN TESTS AND TOXIC GAS EMISSIONS UNDER FLAMING CONDITIONS IN AMERICAN INSTRUMENT CO. SMOKE DENSITY CHAMBER

Laminate No.	I-24A-95				I-24A-119			
Resin	NCNS-12M				NCNS-13P			
Resin Content	22.8%				23.0%			
Federal Aviation Vertical Burn Test 25.853A								
Flame Time	6.2 seconds				8.6 seconds			
Burn Length	1.1 inches				1.2 inches			
Limiting Oxygen Index (LOI)	would not burn in 100% oxygen				would not burn in 100% oxygen			
Smoke Density Dm (Flaming Conditions)	15				20			
Toxic Gas Emissions								
Time in Minutes	5	10	15	20	5	10	15	20
CO, ppm	20	70	110	150	10	30	70	110
HCN, ppm	1	2	5	10	1	2	3.5	5
SO_2, ppm	5	10	10	15	2.5	5	5	5
NO_x, ppm	0.5	1	2	4	0.5	1	2	2

TABLE 46

NCNS-13PE/181E GLASS CLOTH LAMINATES

Laminates	I-24A-124, 124A		I-24A-124B, 124C	
No. of Plies	12		15	
B-Staging Conditions	90°C./1/2 hr		80°C./1/2 hr	
Molding Conditions	350°F./600 psi/1 hr		250°F./600 psi/1/2 hr	
Resin Content	28.3%		26.7%	
Post Cure Conditions	124 400°F./3 hr	124A 400°F./10 hr - 450°F./10 hr	124B 400°F./3 hr	124C 400°F./10 hr - 450°F./10 hr
300°F.. SBS Str., MPa	51	--	65	--
400°F. SBS Str., MPa	--	31	--	42

TABLE 47

CHARACTERIZATION AND PERFORMANCE PROPERTIES OF NCNS-13PE/AS-UNIDIRECTIONAL GRAPHITE FIBER LAMINATE 1-24A-139

Laminating Varnish	90/10 acetone/methanol
Prepreg B-Staging	70°C/30 minutes
No. of Plies	13
Press Laminating Conditions	250°F./600 psi/1 hr
Post Cure Conditions	425°F./7 hr -460°F./8 hr
Resin Solids Content	30.0%
Density	1.58
Fiber Volume	67%
Void Content	Negligible
Initial 350°F. SBS Str., MPa	59
350°F. SBS Str., after 500 hr Oxidative Aging at 350°F., MPa	55
350°F. SBS Str., after 30 day, 95% R.H., 120°F. Humidity Aging, MPa	38
300°F. SBS Str., after 30 day, 95% R.H., 120°F. Humidity Aging, MPa	64

TABLE 48

CHARACTERISTICS OF EPOXY RESINS REACTED WITH NCNS-13P RESIN

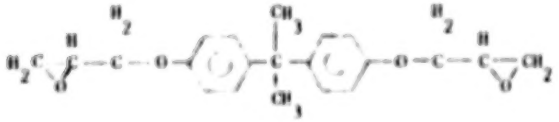
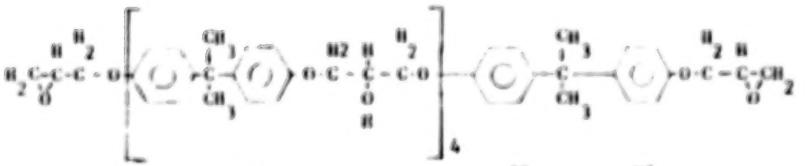
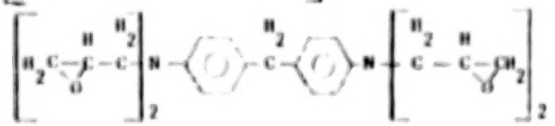
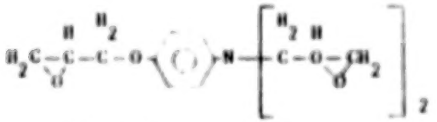
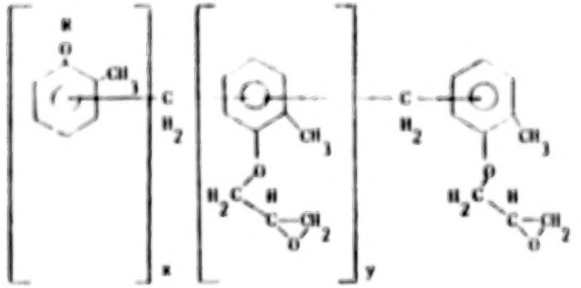
Resins		M.P. °C	Wt. per Epoxy
6010		liquid	190
GT 7014		94	76?
MY 720		liquid	125
0500		liquid	110
ECN 1273		73	225

TABLE 49

LABORATORY NCNS-13P RESIN BLENDS WITH VARIOUS ARALDITE EPOXY RESINS

Run No.	I-25R-36	I-25R-37A	I-25R-46A	I-25R-50C
Epoxy Resin	6010	6010	GT 7014	GT 7014
Epoxy Resin Concentration	20%	20%	20%	20%
Laminating Varnish	20/80 methanol/ methyl acetate	20/80 methanol/ methyl acetate	20/80 methanol/ methyl acetate	20/80 methanol methyl acetate
Prepreg	181E glass cloth	181E glass cloth	181E glass cloth	unidirectional AS graphite fiber
B-Staging Conditions	70°C/1 hr	25°C/24 hr + 70°C/1 hr	90°C/1 hr	85°C/1 hr
Press Laminating Conditions	250°F/600 psi/1 hr	250°F/600 psi/1 hr	250°F/600 psi/1 hr	250°F/600 psi/1 hr
Resin Melt Flow	1/4" from 17 plies	1/8" from 17 plies	1/8" from 15 plies	1/4" from 7 plies
Post Cure Conditions	425°F/3 hr	425°F/10 hr	425°F/3 hr	400°F/10 hr
Resin Solids Concentration	23.4%	27.0%	30.7%	44.0%
400°F Short Beam Shear Strength, MPa	57	36	38	61

TABLE 49 (Cont.)

LABORATORY NCNS-13P RESIN BLENDS WITH VARIOUS ARALDITE EPOXY RESINS

Run No.	I-25R-53	I-25R-57A	I-25R-60	I-25R-61
Epoxy Resin	MY 720	MY 720	0500	ECN 1273
Epoxy Resin Concentration	10%	10%	10%	10%
Laminating Varnish	acetone	acetone	acetone	acetone
Prepreg	181E glass cloth	unidirectional AS graphite fiber	181E glass cloth	181E glass cloth
B-Staging Conditions	60°C/1 hr	60°C/30 min	75°C/1 hr	70°C/1 hr
Press Laminating Conditions	200°F/600 psi/1 hr	250°F/600 psi/1 hr	250°F/600 psi/1 hr	250°F/600 psi/1 hr
Resin Melt Flow	negligible from 15 plies	1/8" from 12 plies	1/2" from 15 plies	5/8" from 15 plies
Post Cure Conditions	400°F/10 hr	400°F/10 hr	400°F/10 hr	400°F/10 hr
Resin Solids Concentration	23.4%	38.5%	27.6%	26.9%
400°F Short Beam Shear Strength, MPa	54	103 @ 350°F	63	58

TABLE 50

NCNS-13P-CY 179 RESIN/AS GRAPHITE FIBER UNIDIRECTIONAL LAMINATES

Laminate No.	I-25R-89	I-25R-98	I-25R-100	I-25R-106	I-25R-111
CY 179 Conc.	10%	5%	5%	10%	5%
Vacuum Bag-Autoclave Processing Conditions	1) Apply high vacuum for 1 hour at R.T. 2) Heat to 140°F. in 15 mins. and then apply 100 psi pressure. 3) Heat to 400°F. in 50 mins. 4) Cure 1 hour at 400°F.	1) Apply high volume for 1 hour at R.T. 2) Heat to 158°F. in 20 mins. and then apply 100 psi pressure. 3) Heat to 400°F in 45 mins. 4) Cure 2 hours at 400°F.	1) Apply high vacuum for 1 hour at R.T. 2) Heat to 194°F. in 25 mins. and then apply 100 psi pressure. 3) Heat to 400°F. in 40 mins. 4) Cure 4 hours at 400°F.	1) Apply high vacuum for 1 hour at R.T. 2) Heat to 140°F. in 15 mins. and then apply 100 psi pressure. 3) Maintain 30 min. @ 140°F. and then heat to 400°F. in 50 mins. 4) Cure 3 hours at 400°F.	1) Apply high vacuum for 1 hour at R.T. 2) Heat to 194°F. in 25 mins. and then apply 100 psi pressure. 3) Heat to 400°F. in 40 mins. 4) Cure 4 hours at 400°F.
Post Cure Conditions	400°F./10 hrs.	400°F./10 hrs.	400°F./24 hrs.	400°F./24 hrs.	400°F./24 hrs.
Resin Flow	18%	41%	26%	38%	34%
Resin Content	41.0%	31.0%	38.3%	35.6%	35.8%
Fiber Volume	53%	64%	57%	55%	56%
Void Content	none	none	none	3.3%	0.8%
350°F. Short Beam Shear Str., MPa	48	58	62	61	65
350°F. Short Beam Shear Str., after 30 day 95% R.H., 120°F. Humidity Exposure, MPa	54	--	45	--	--

TABLE 51

POST CURE STUDY ON NCNS-13P-EPOXY RESIN LAMINATES

Run No.	I-25R-53	I-25R-57	I-25R-61	I-25R-100
Resin Composition	90% NCNS-13P/ 10% MY 720	90% NCNS-13P/ 10% MY 720	90% NCNS-13P/ 10% ECN 1273	95% NCNS-13P/ 5% CY 179
Fiber Reinforcement	181E glass cloth	AS graphite fiber	181E glass cloth	AS graphite fiber
Fabrication Process	press lamination	press lamination	press lamination	vacuum bag-autoclaving
Resin Content	33.4%	38.5%	26.9%	38.3%
Fiber Volume	--	56.5%	--	56.7%
Short Beam Shear Strength after				
400°F/10 hr. Post Cure, MPa	54 @ 400°F	103 @ 350°F	58 @ 400°F	61 @ 350°F
425°F/3 hr. Post Cure, MPa	--	--	--	48 @ 350°F
460°F/6 hr. Post Cure, MPa	32 @ 400°F	63 @ 400°F	52 @ 400°F	heat distorted

TABLE 52

NCNS-12 DAPI RESIN LAMINATES

Laminate No.	I-22F-120	I-22F-119
Reinforcement	HT-S graphite fiber-unidirectional	181E glass fabric
Lay-up	11 plies 4" x 5"	12 plies 4" x 4"
B-Staging Conditions	70°C/1 hr -100°C/15 min	70°C/1 hr -90°C/15 min
Press Laminating Conditions	350°F/1.5 hr -400°F 1 hr /600 psi	400°F/600 psi/2 hr
Post Curing Conditions	435°F/2 hr	435°F/2 hr
Void Content	0%	0%
Resin Content	40.5%	26.2%
Fiber Volume	55%	58%
400°F Flexural Strength, MPa	842	439
400°F Flexural Modulus, MPa	84,500	19,300
400°F SBS Strength, MPa	39 44 (450°F post cure)	36 --
350°F SBS Strength, MPa	50 50 (450°F post cure)	-- --

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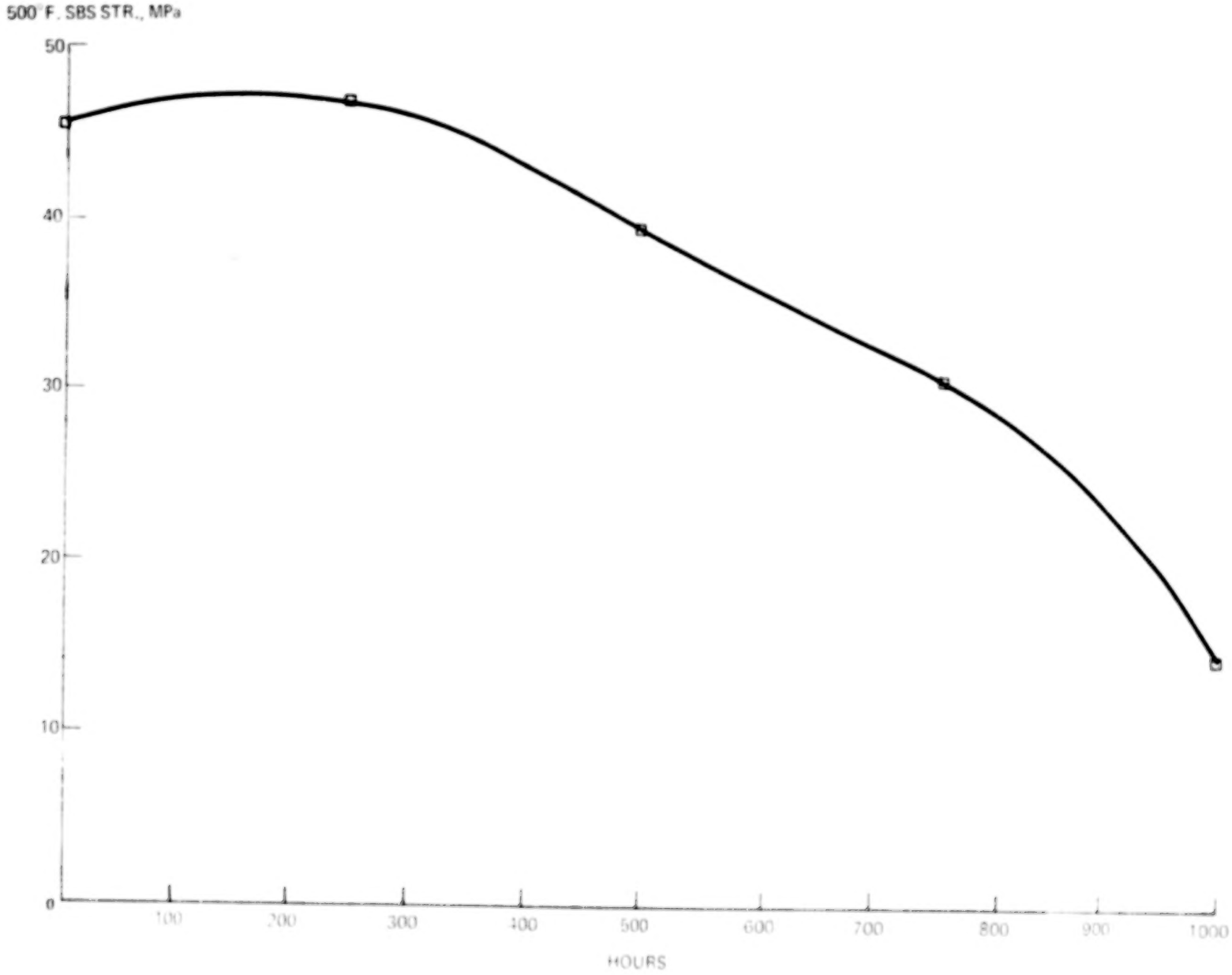

FIGURE 1 – 500°F. OXIDATIVE AGING OF P105A-181E GLASS LAMINATE I-22F-28

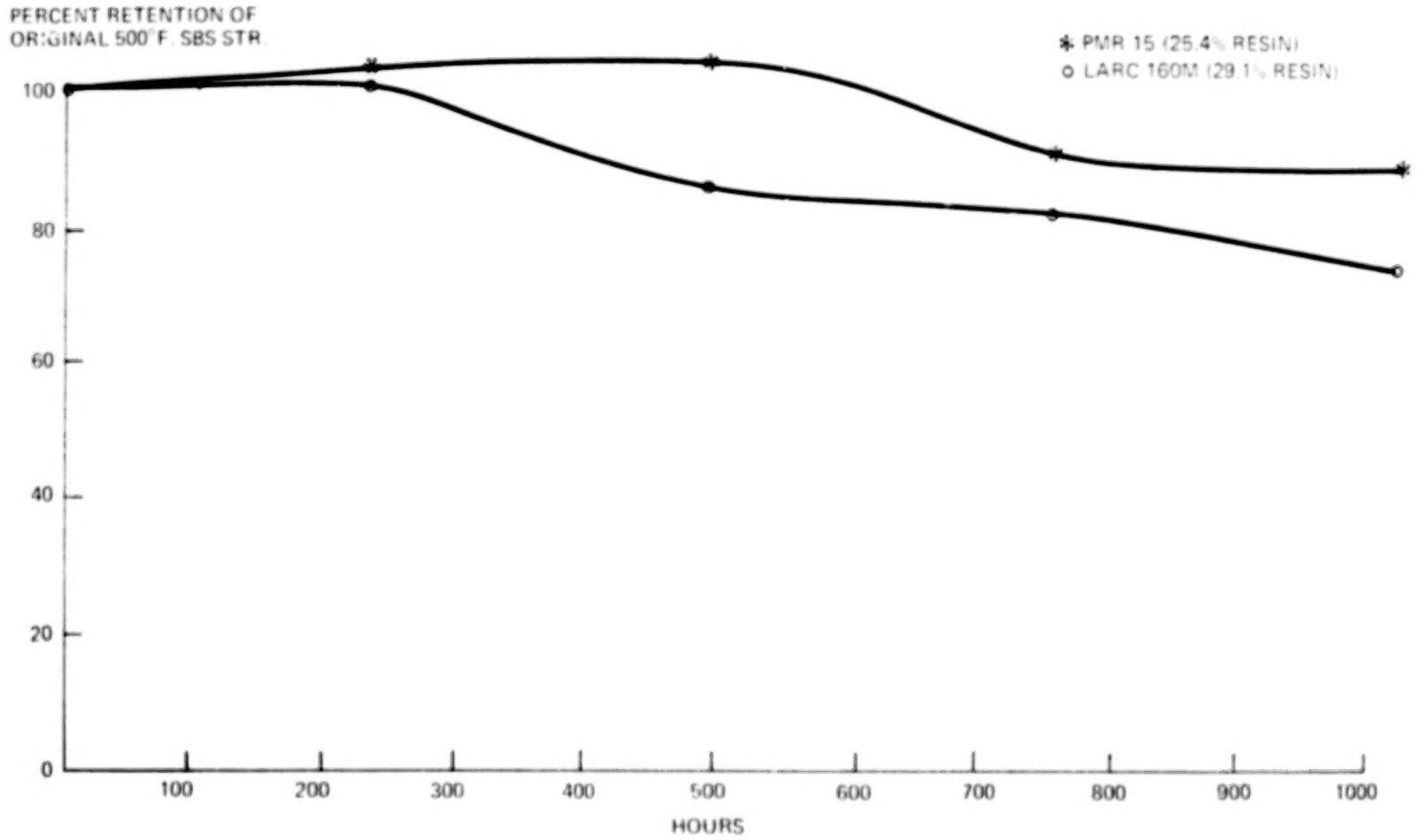

FIGURE 2 – 500°F. OXIDATIVE AGING OF PMR 15 I-24A-47 AND LARC 160M I-22F-128 GLASS FABRIC LAMINATES

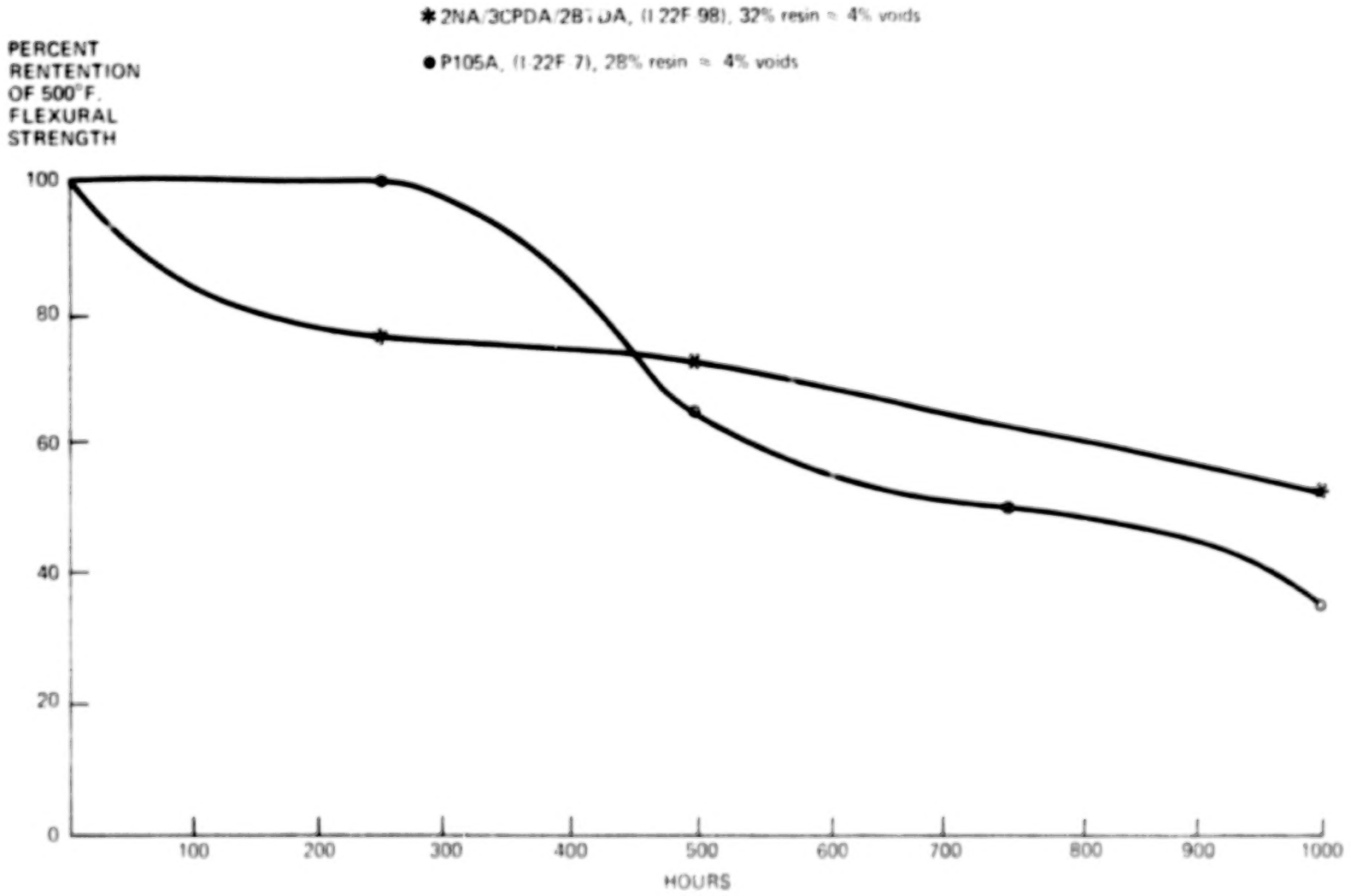

FIGURE 3 – OXIDATIVE AGING AT 500°F. OF 550°F. AUTOCLAVABLE POLYIMIDE 181E GLASS LAMINATES

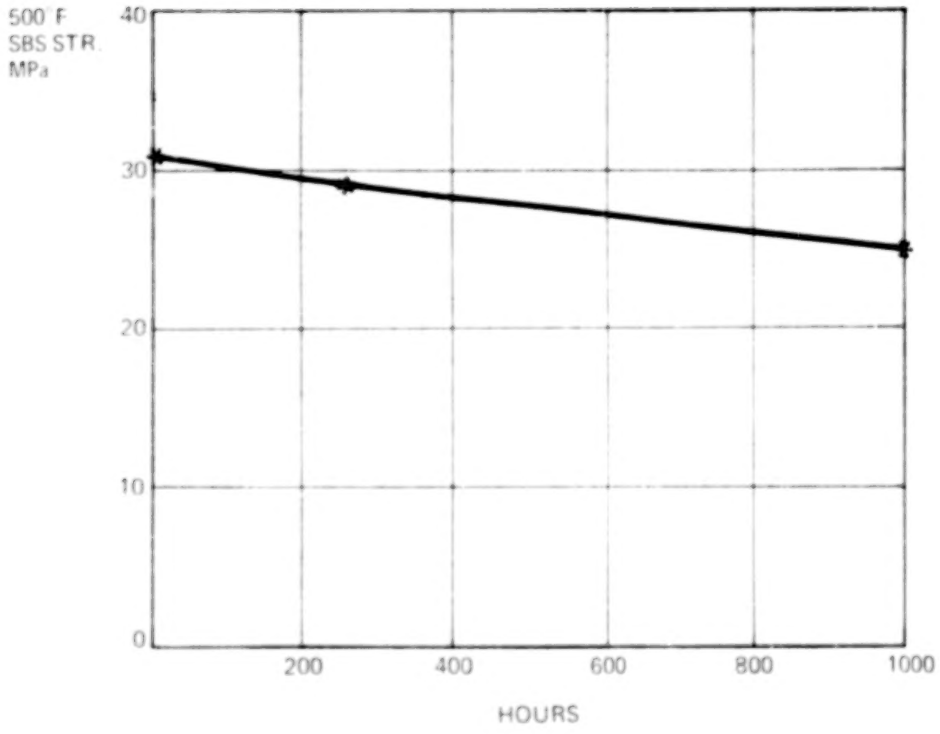

FIGURE 4 – 500°F. OXIDATIVE AGING OF LAMINATE I-22F-106

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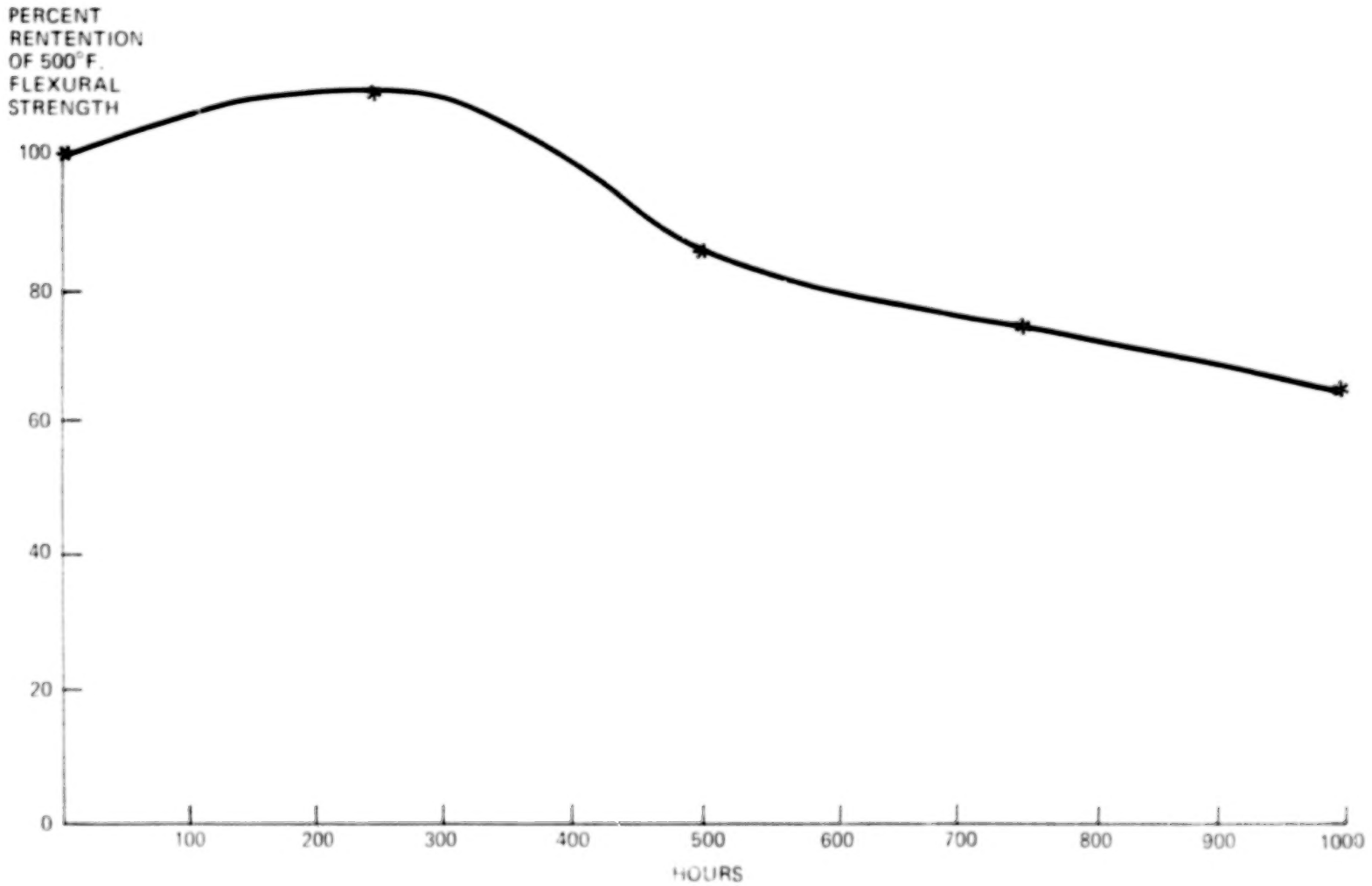

FIGURE 5 – 500°F. OXIDATIVE AGING OF 2NE/3DAT/2BTDE/181E GLASS LAMINATE I 22F 30

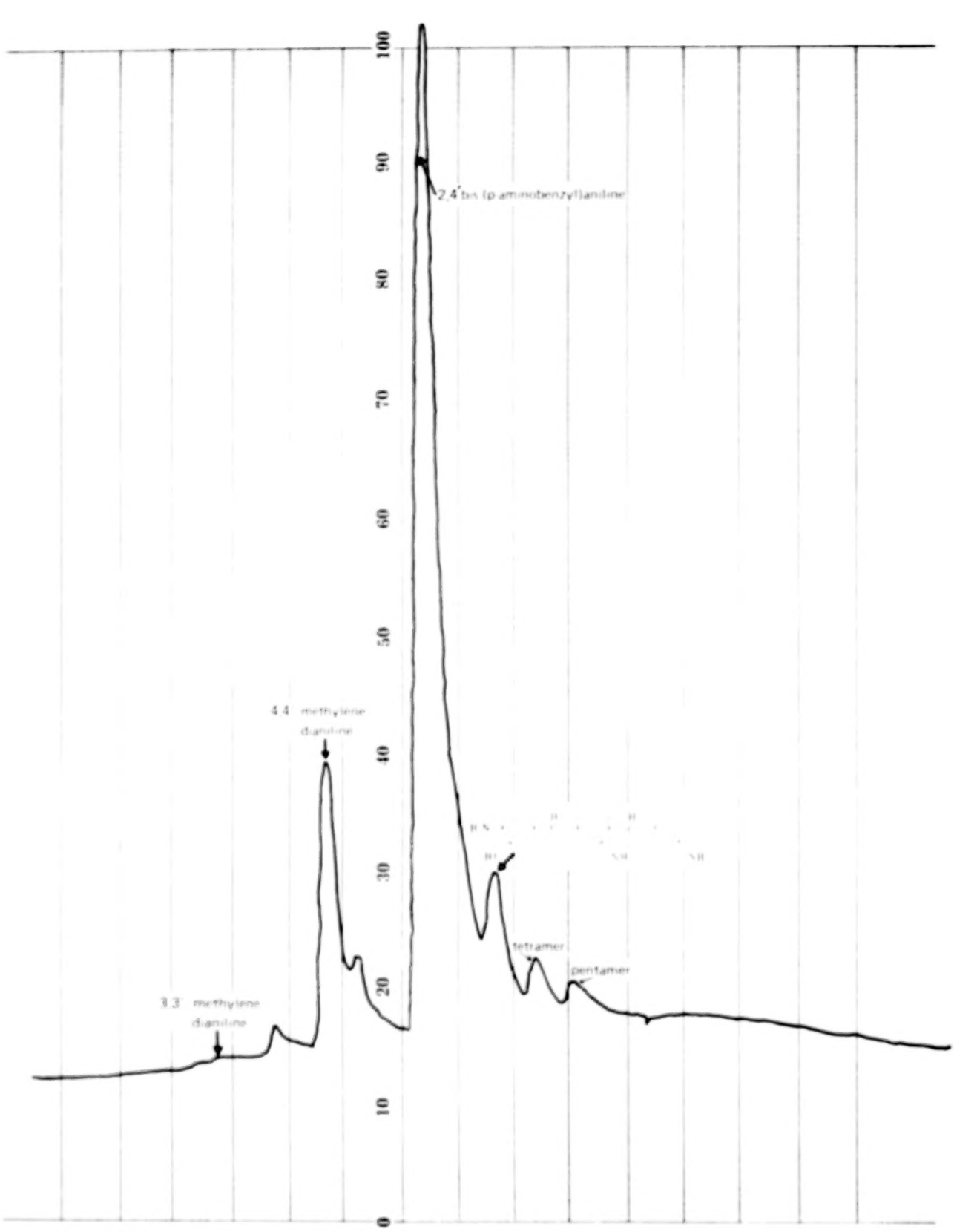

FIGURE 6 – LIQUID CHROMATOGRAM OF BABA MIXTURE 578/1159-1161

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PAGE

INST 5 METHOD 21 A% ET

FLAME DUMMY FOR AREA%

PEAK NO	NAME	TYPE	COMP W%	TIME SEC	CORR TIME	AREA %	FACTOR
1	UNEXP		OE+OO	818	1072	0.0297	1000
2	UNEXP		OE+OO	854	1119	3.8042	1000
3	UNEXP		OE+OO	918	1203	0.0649	1000
4	UNEXP		OE+OO	1396	1830	0.0732	1000
5	UNEXP	P	OE+OO	1441	1889	2.0833	1000
6	MAJOR	P	OE+OO	1526	2000&	78.4203	1000
7	UNEXP	PB	OE+OO	1577	2067	0.3299	1000
8	UNEXP		OE+OO	1683	2206	0.2079	1000
9	UNEXP		OE+OO	1949	2554	14.7402	1000
10	UNEXP	P	OE+OO	2715	3558	0.0564	1000
11	UNEXP	P	OE+OO	2853	3739	0.0408	1000
12	UNEXP	PB	OE+OO	2872	3764	0.1490	1000

TOTAL AREA 855010

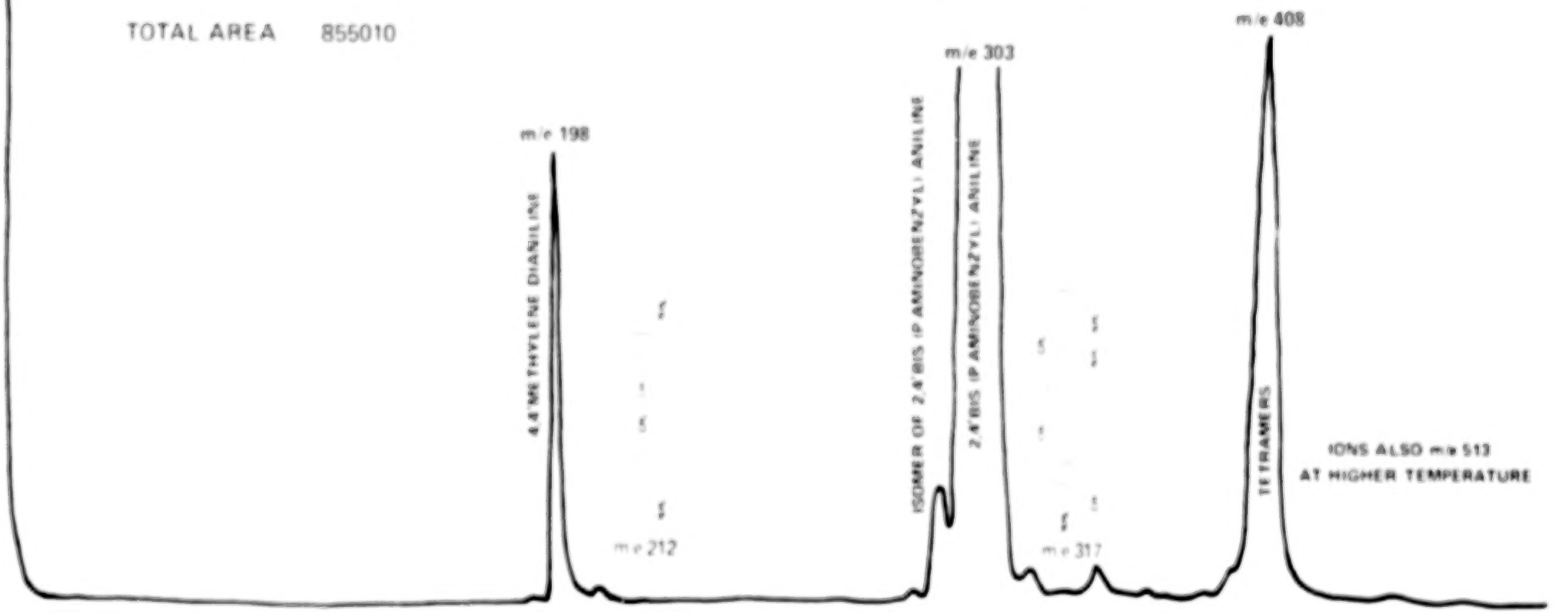

FIGURE 7 – GC/DIRECT PROBE MS ANALYSIS OF BABA MIXTURE AL-671-143

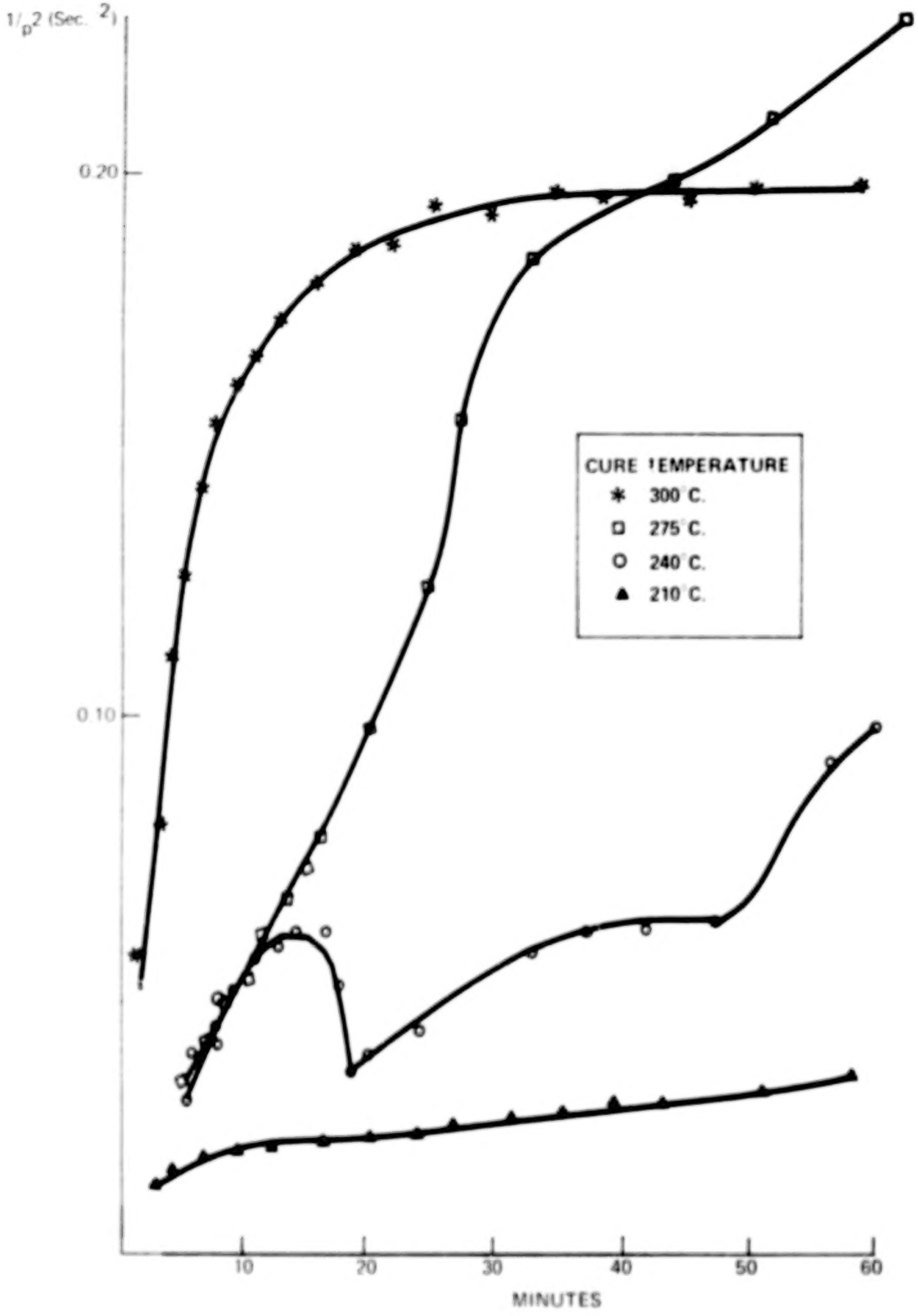

FIGURE 8 – TBA CURING STUDY ON 4/2/1 IMIDE PREPOLYMER – – APPARENT RIGIDITY VS TIME

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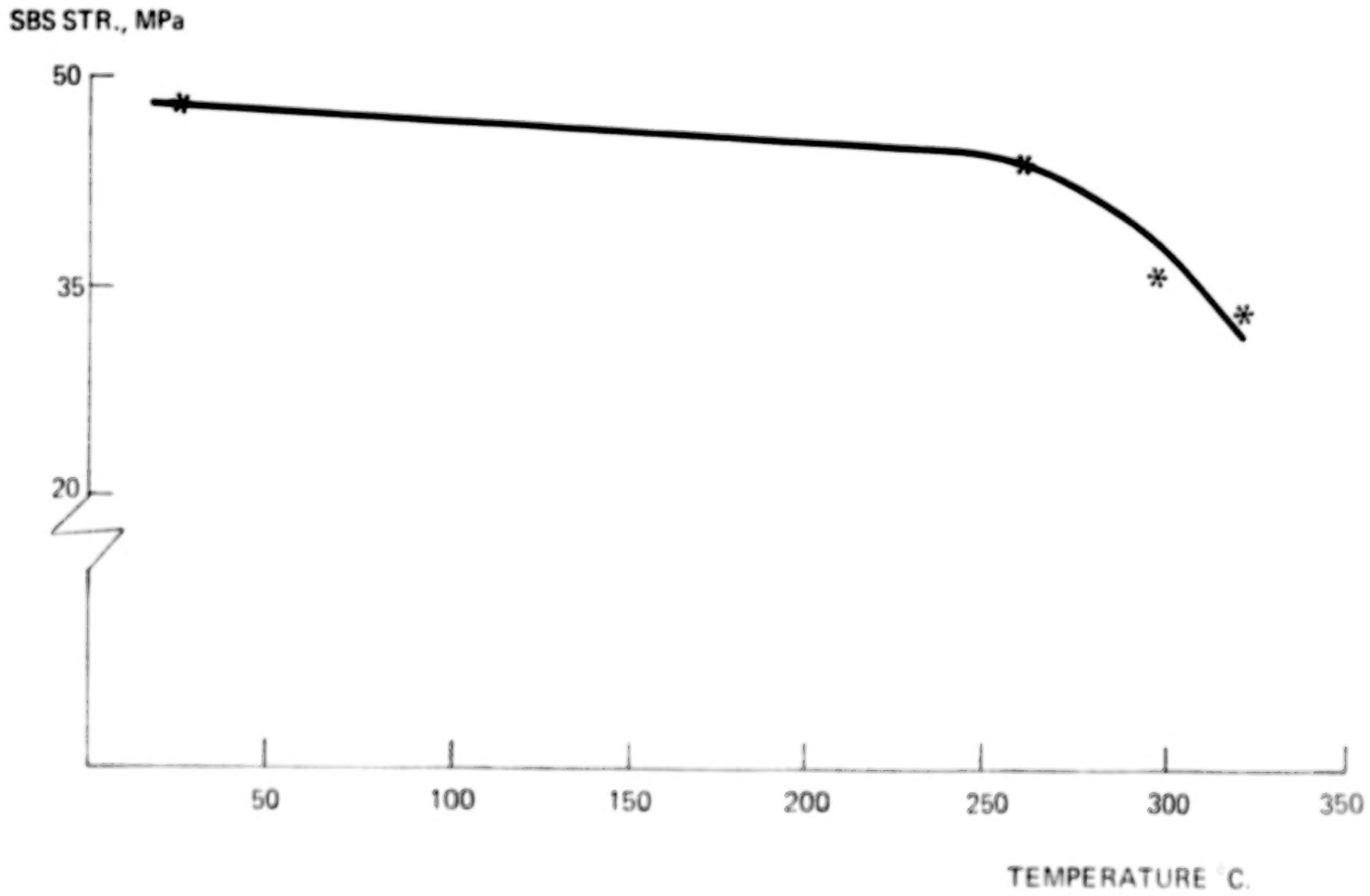

FIGURE 9 – INTERLAMINAR SHEAR STRENGTH VS TEMPERATURE OF GLASS CLOTH LAMINATE I 25R 28

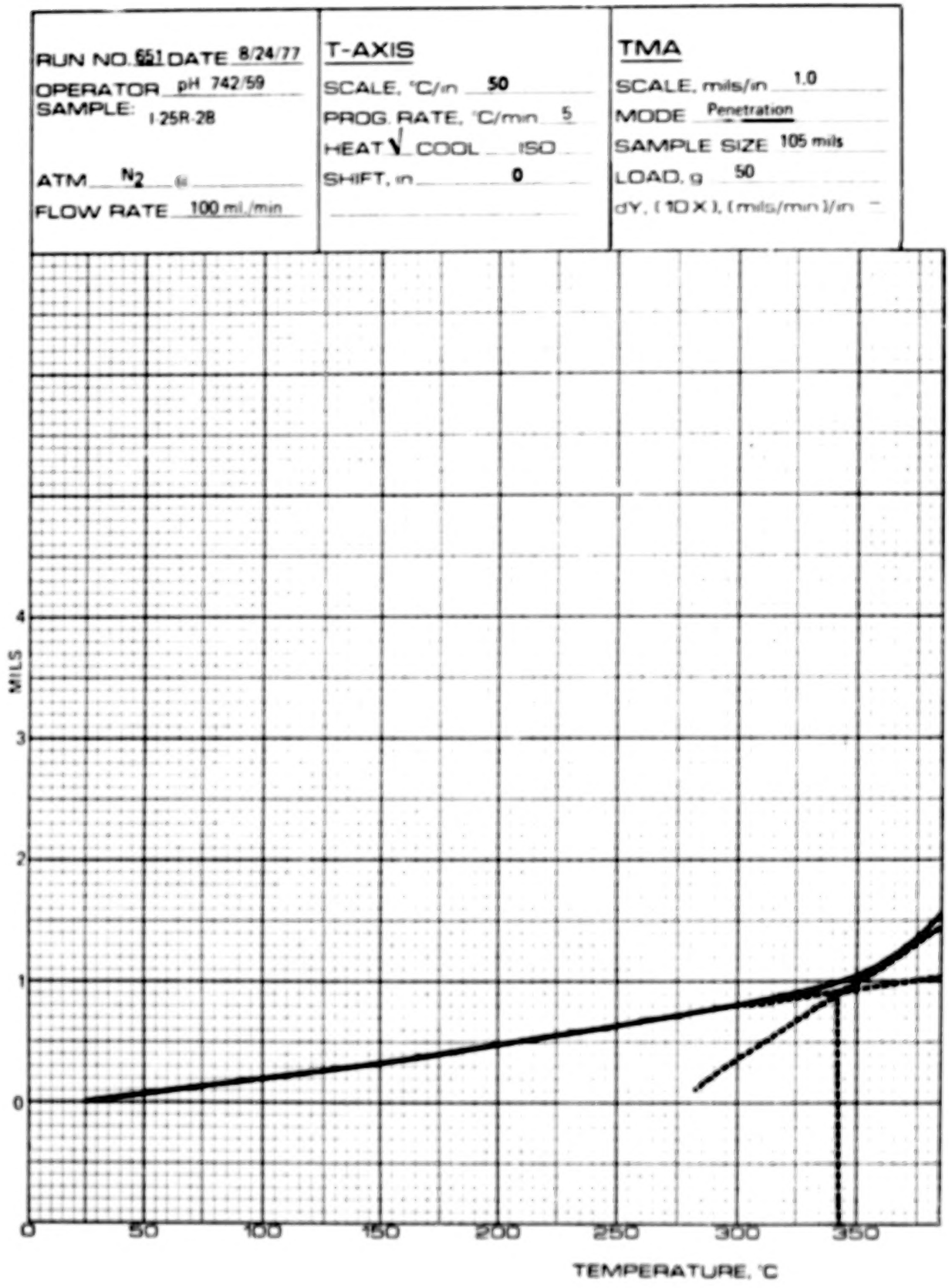

FIGURE 10 – THERMAL EXPANSION IN Z-AXIS OF GLASS CLOTH LAMINATE I-25R-28

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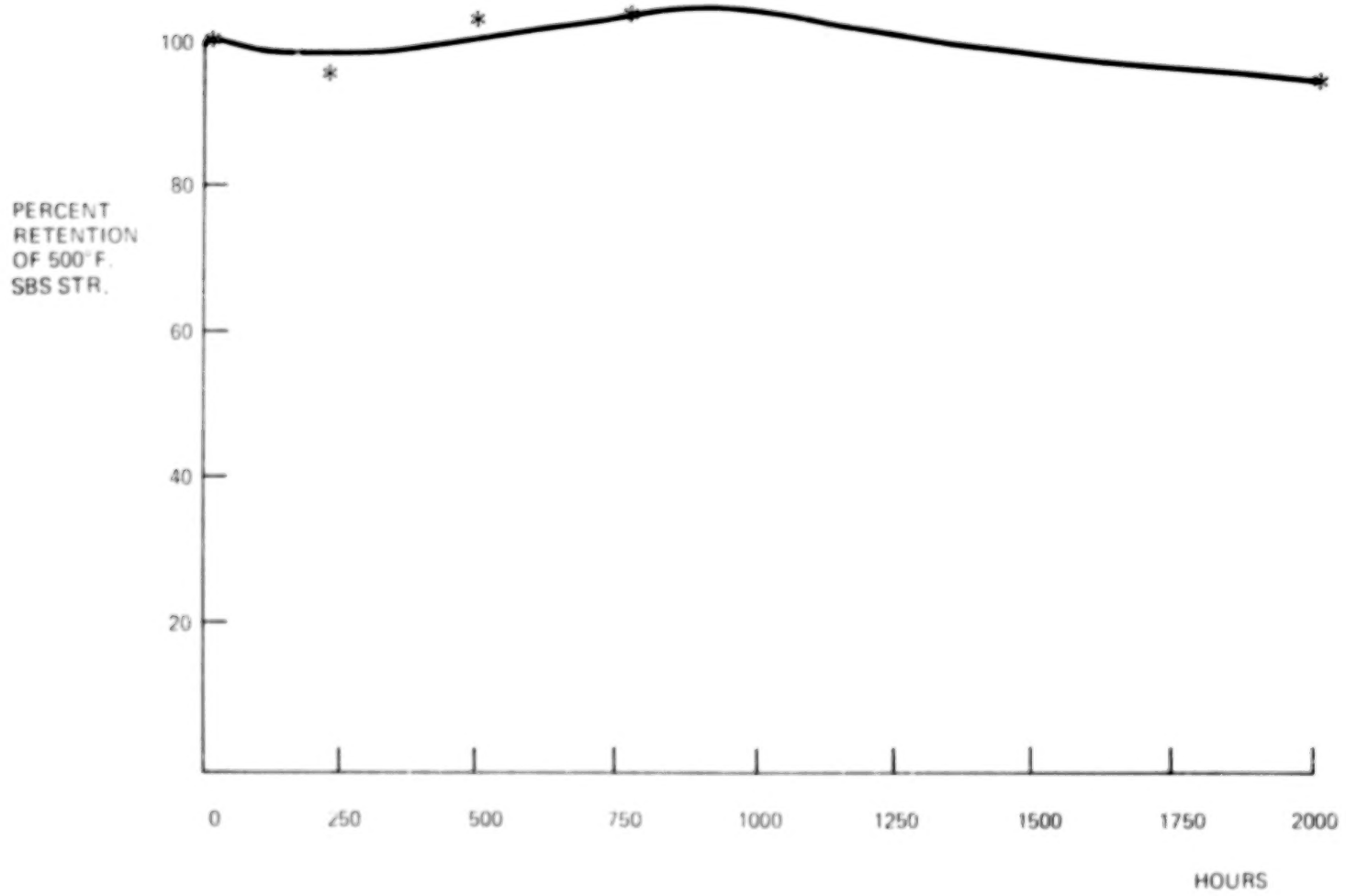


FIGURE 11 – 500°F. OXIDATION AGING OF AS UNIDIRECTIONAL GRAPHITE FIBER LAMINATE I 24A 102

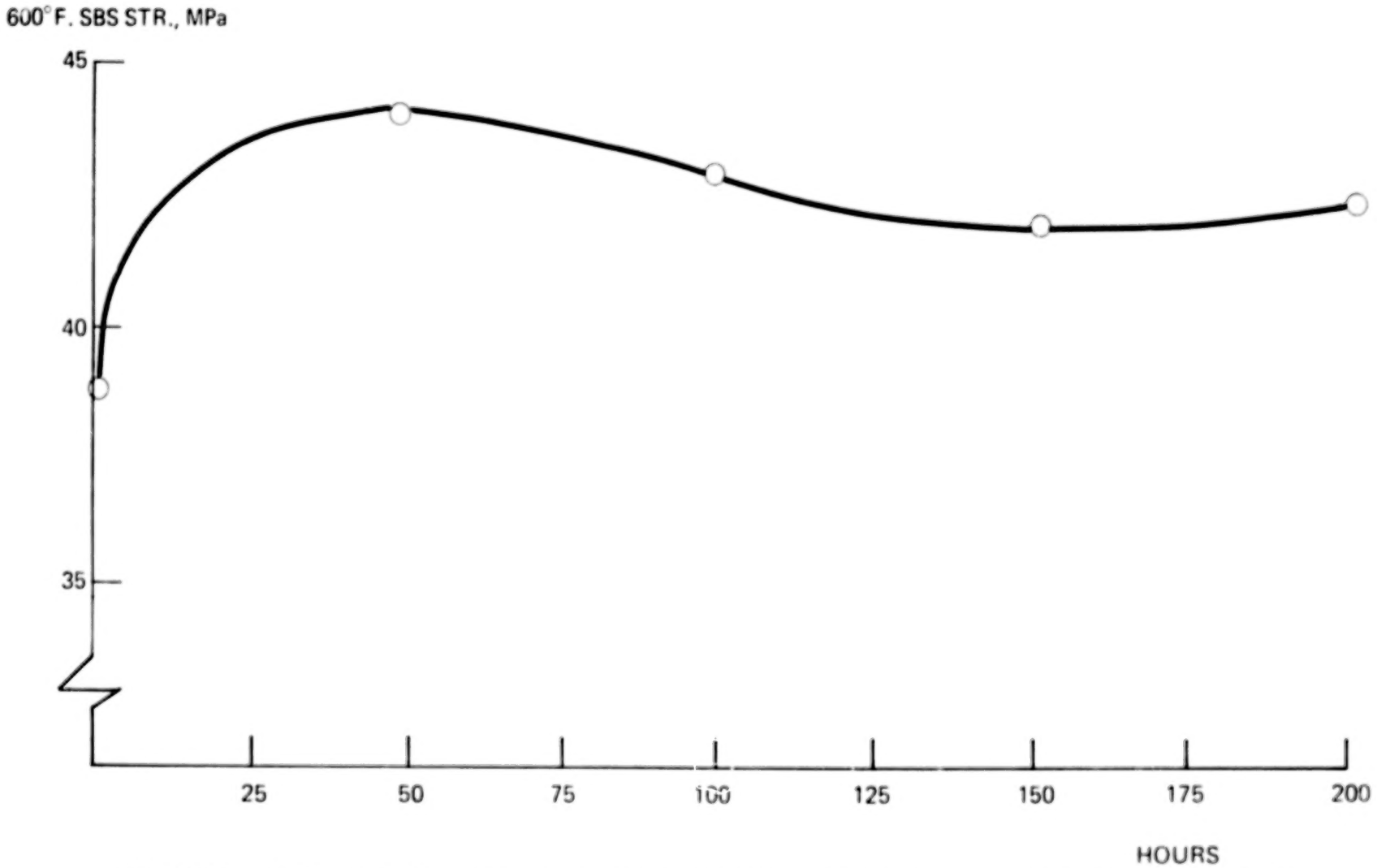
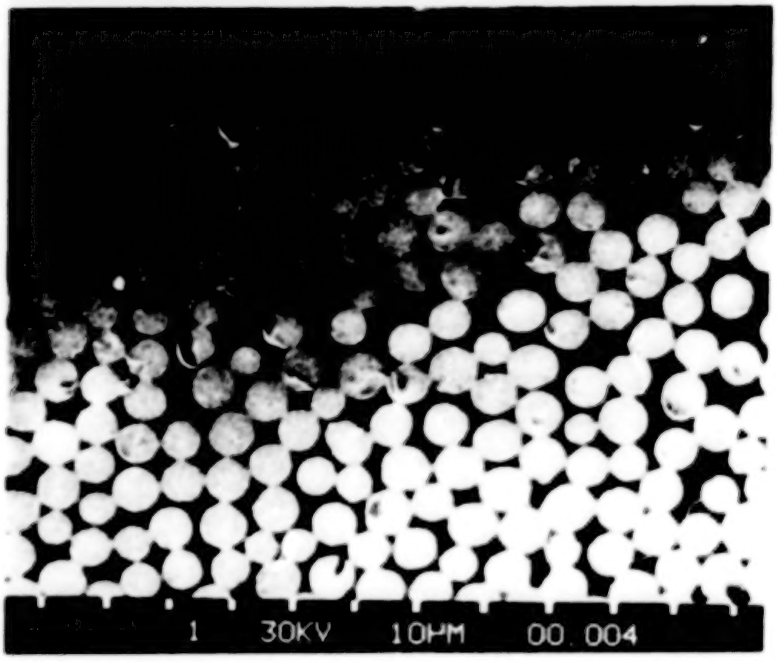


FIGURE 12 – 600° F. OXIDATIVE AGING OF HT-S UNIDIRECTIONAL GRAPHITE FIBER LAMINATE I-24A-118



1000 X

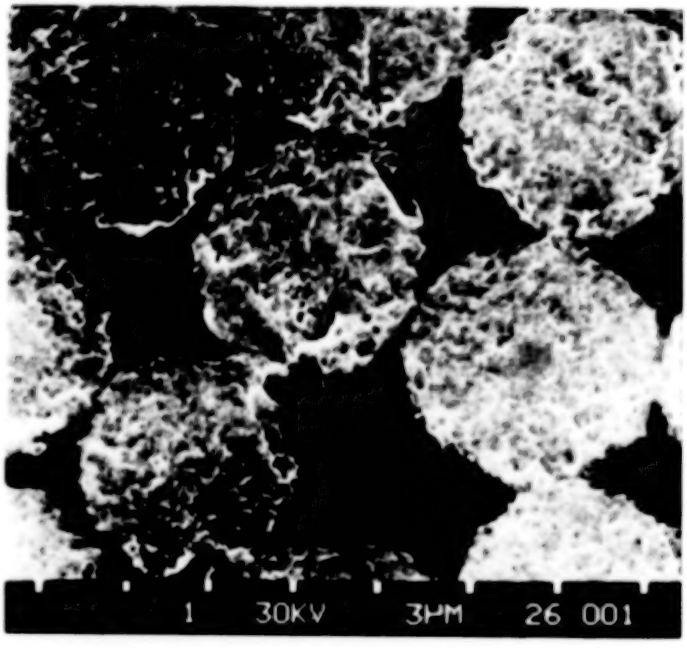


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FIGURE 13

SEM PHOTOMICROGRAPHS OF CROSS SECTIONS

OF LAMINATE I - 25R - 151

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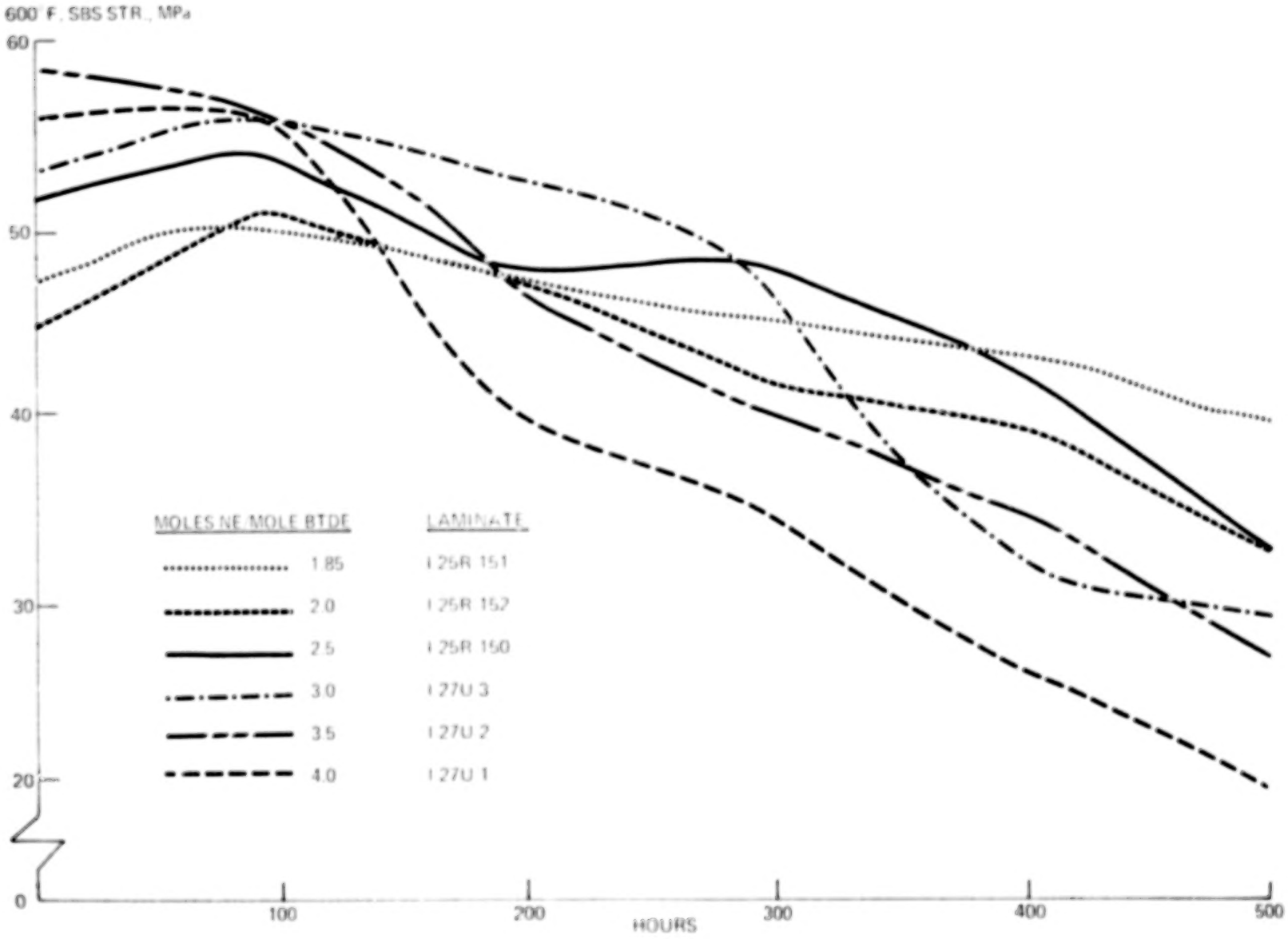

FIGURE 14 – 600°F. OXIDATIVE AGING OF LAMINATES WITH VARYING CONCENTRATIONS OF ADDITION POLYMERIZABLE NADIC GROUPS

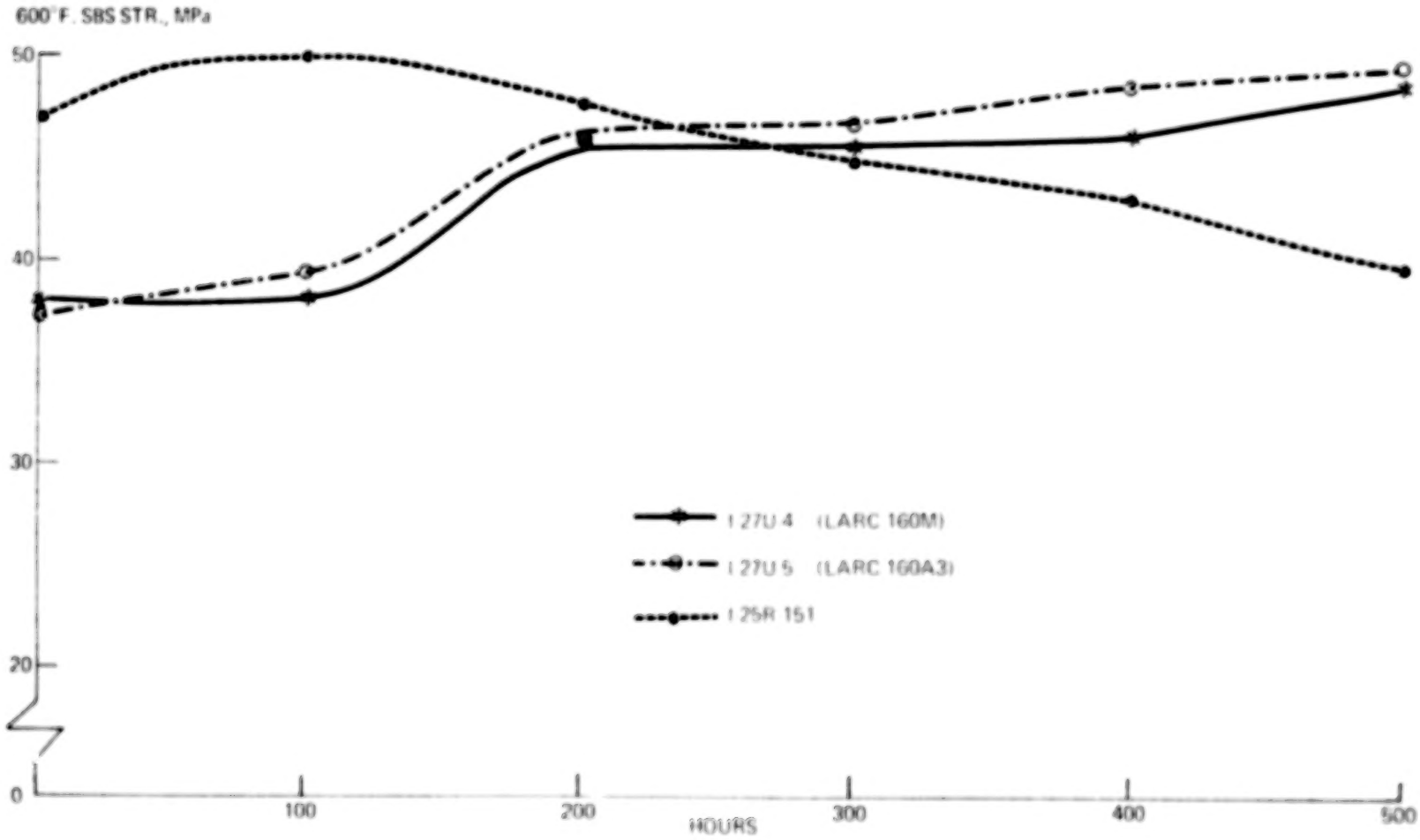

FIGURE 15 – 600°F. OXIDATIVE AGING OF LAMINATES I-27U-4, I-27U-5 AND I-25R-151

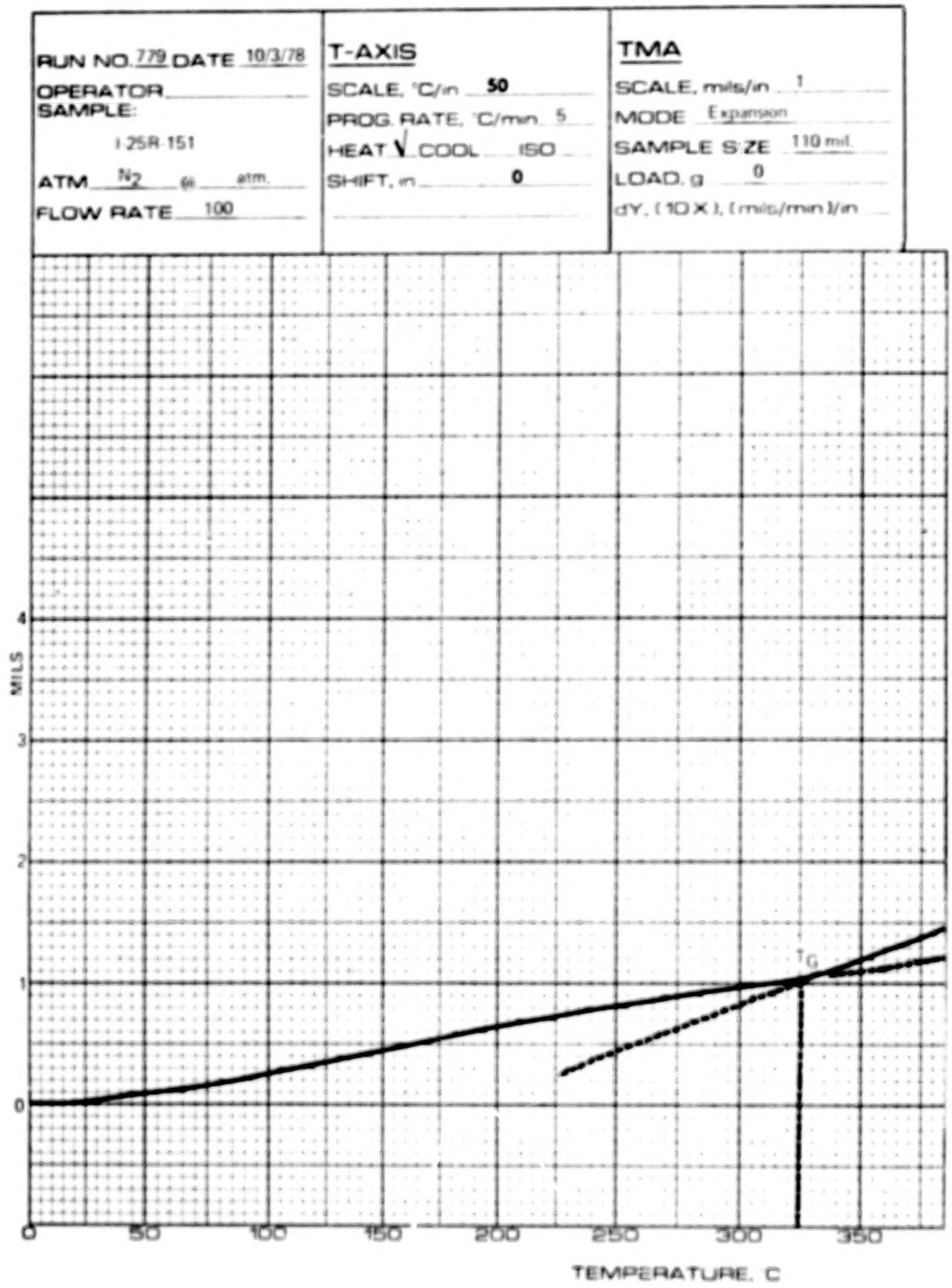

FIGURE 16 – Z-AXIS THERMAL EXPANSION OF 1-25R-151 POLYMIDE/CELION 6000 UNIDIRECTIONAL GRAPHITE FIBER LAMINATE

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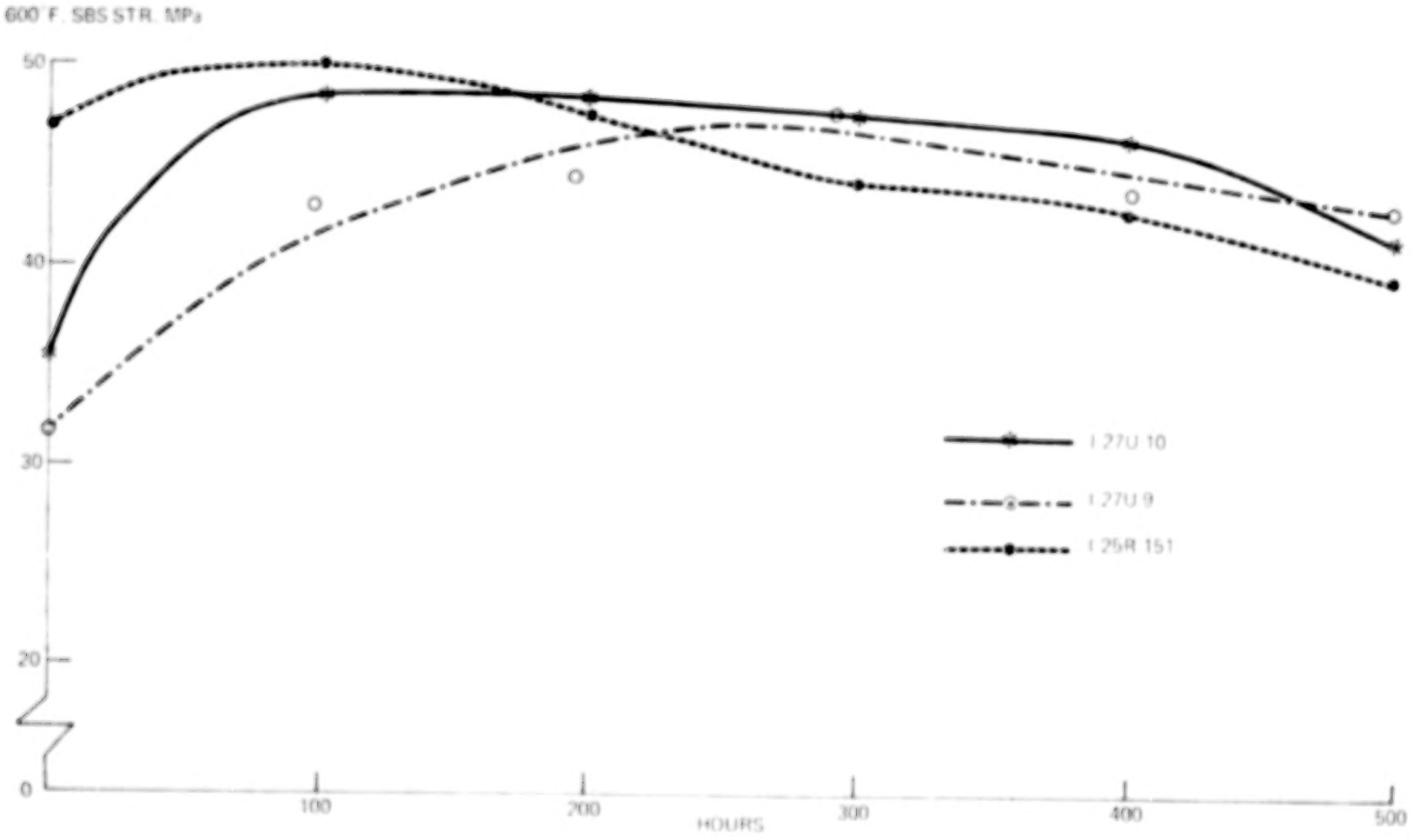


FIGURE 17 – 600°F. OXIDATIVE AGING OF LAMINATES I 27U 9, I 27U 10 AND I 25R 151

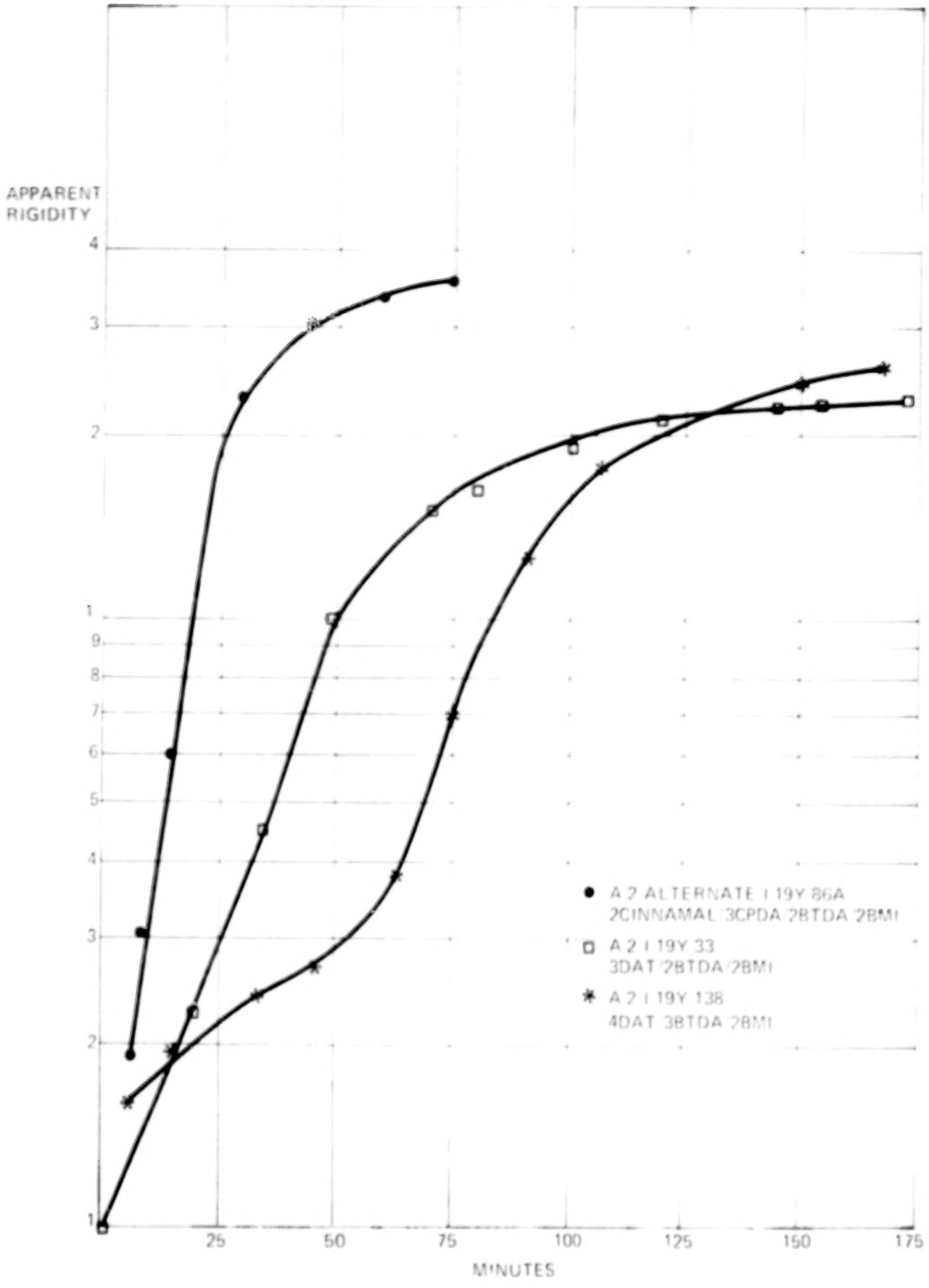


FIGURE 18 – APPARENT RIGIDITY VS. TIME FOR 400°F. AUTOCLAVE POLYIMIDES–CURE TEMPERATURE 400°F.

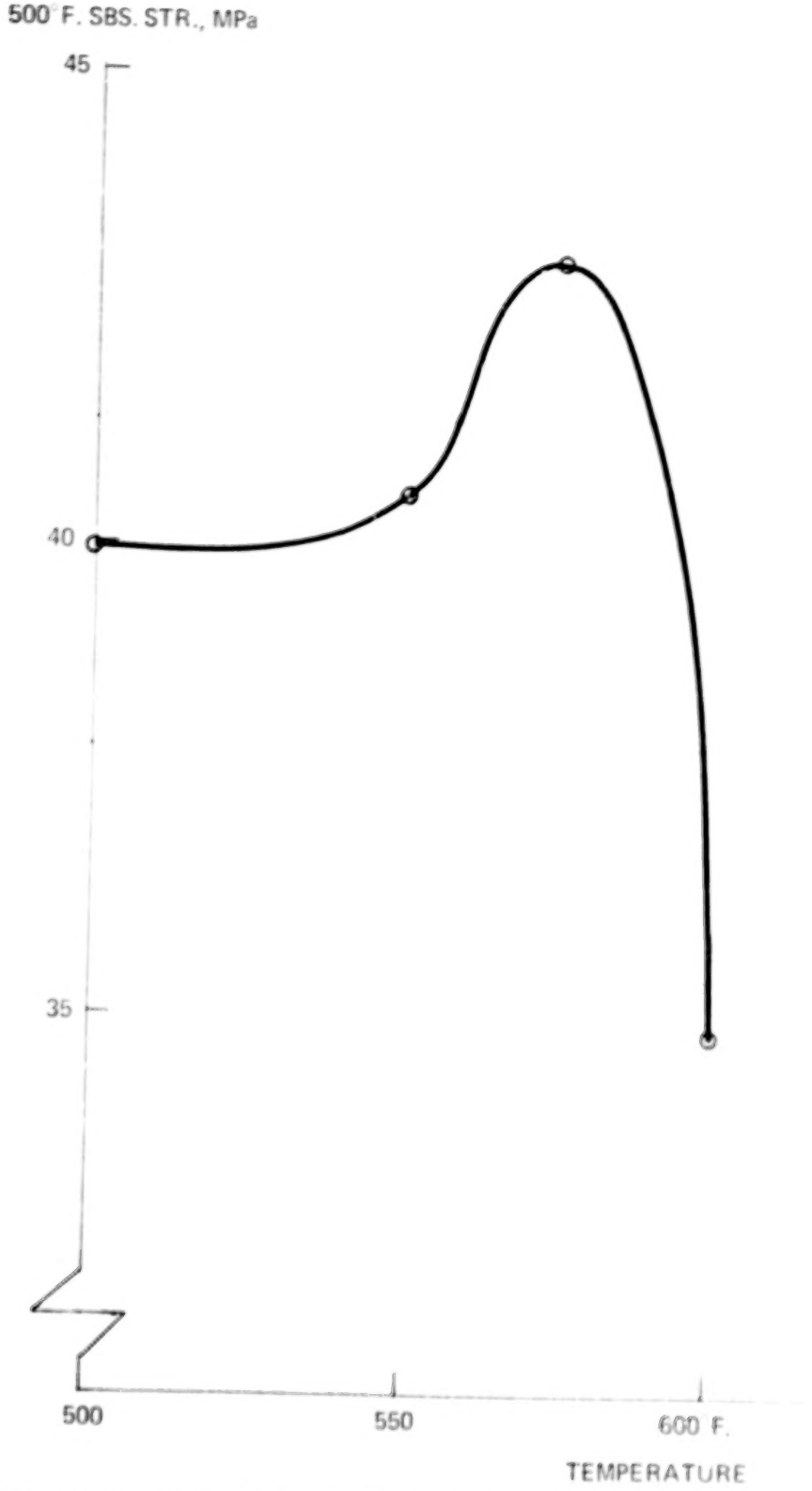


FIGURE 19 – A-2 ALTERNATE-181E GLASS FABRIC LAMINATE I-19N-124 POST CURING STUDIES

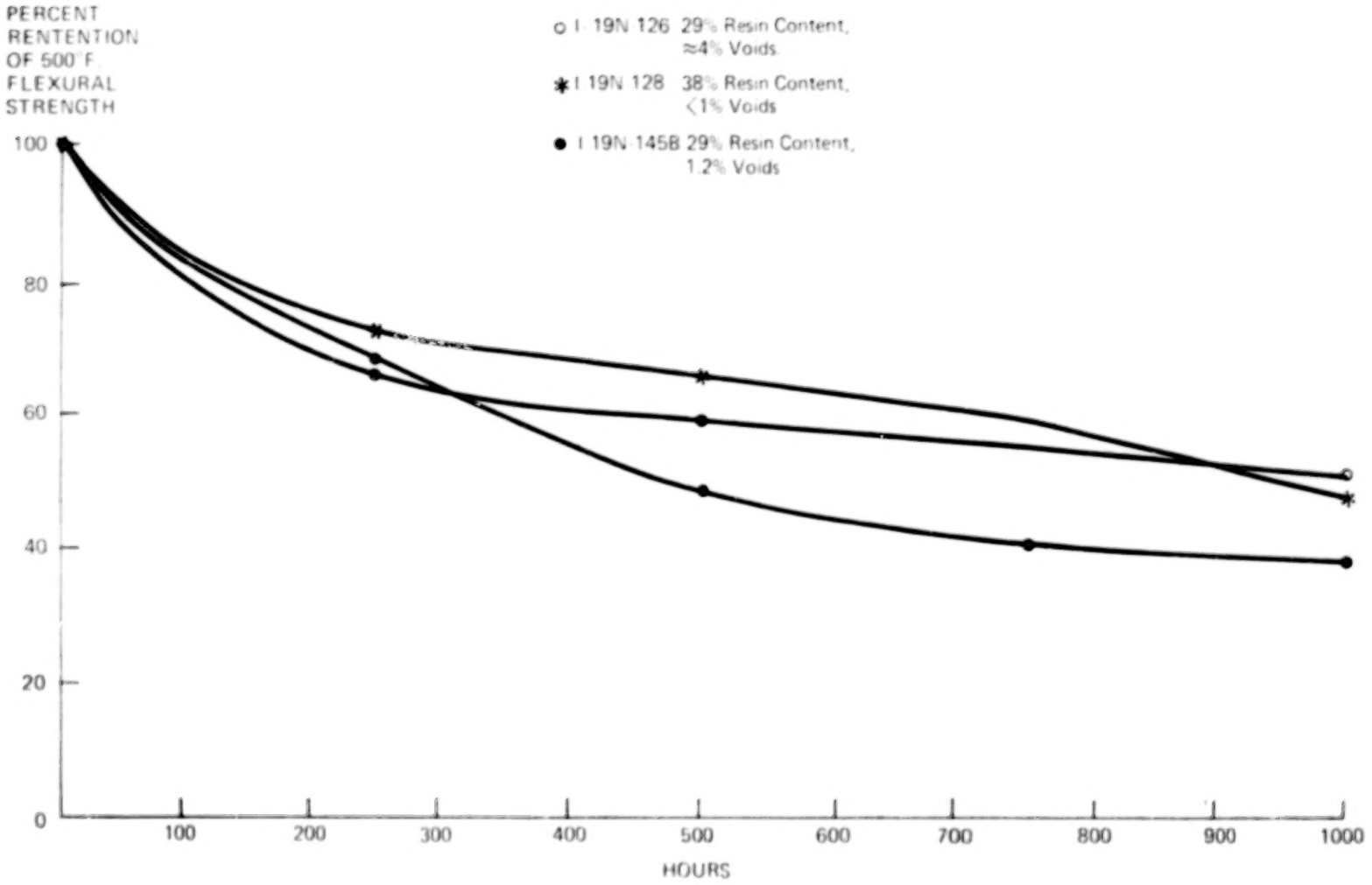


FIGURE 20 – OXIDATIVE AGING AT 500°F. OF A 2 ALTERNATE-181E GLASS LAMINATES

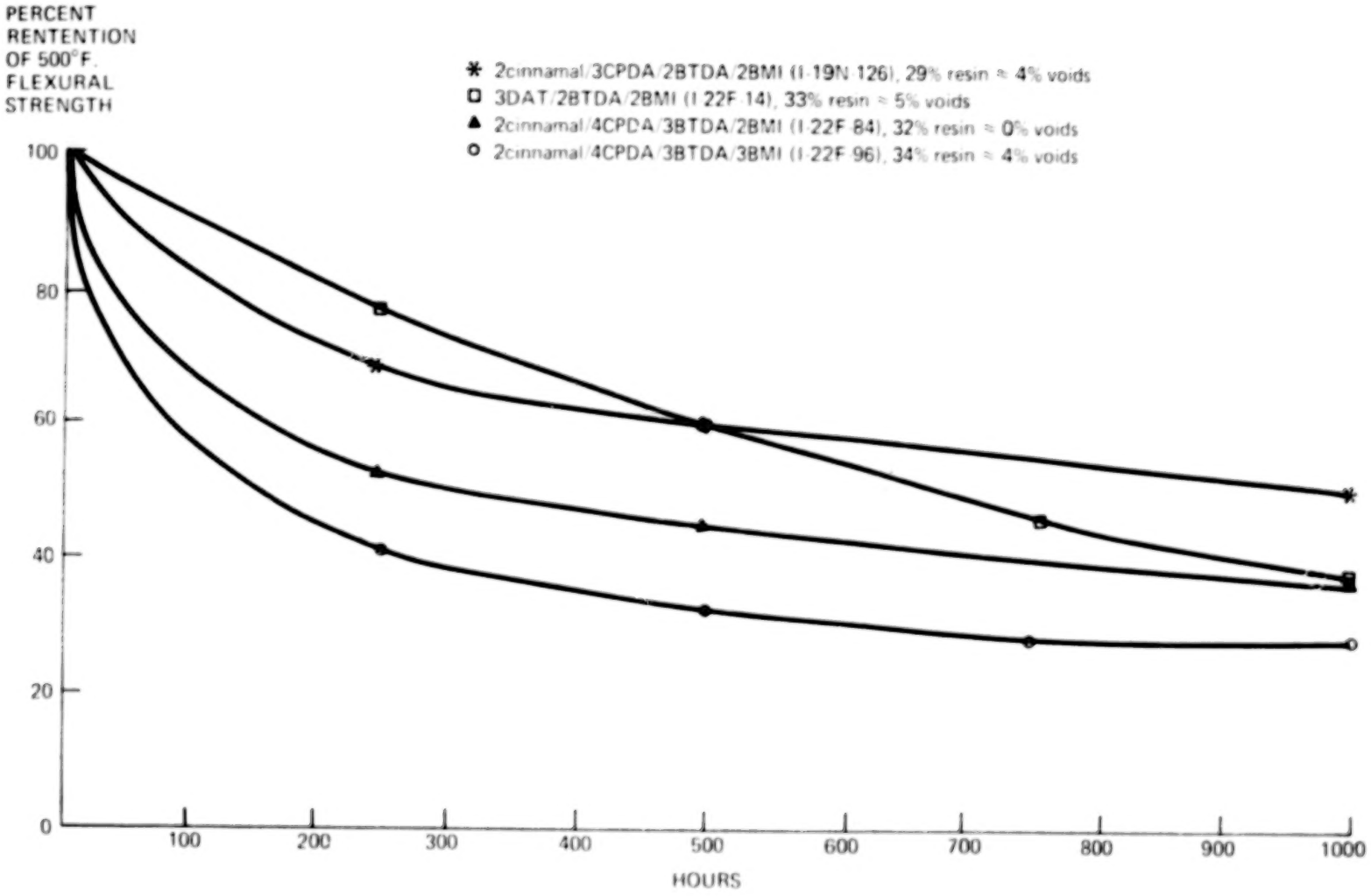


FIGURE 21 – OXIDATIVE AGING AT 500°F. OF 400°F. AUTOCLAVABLE POLYMIDE-181E GLASS LAMINATES

SMOKE DENSITY TEST

REQ. No. _____

Budget Ctr. RE 8060

Sample No.: I-24A-95

Date 6/10/77

Sample Description: NCNS-12M/181E GLASS LAMINATE

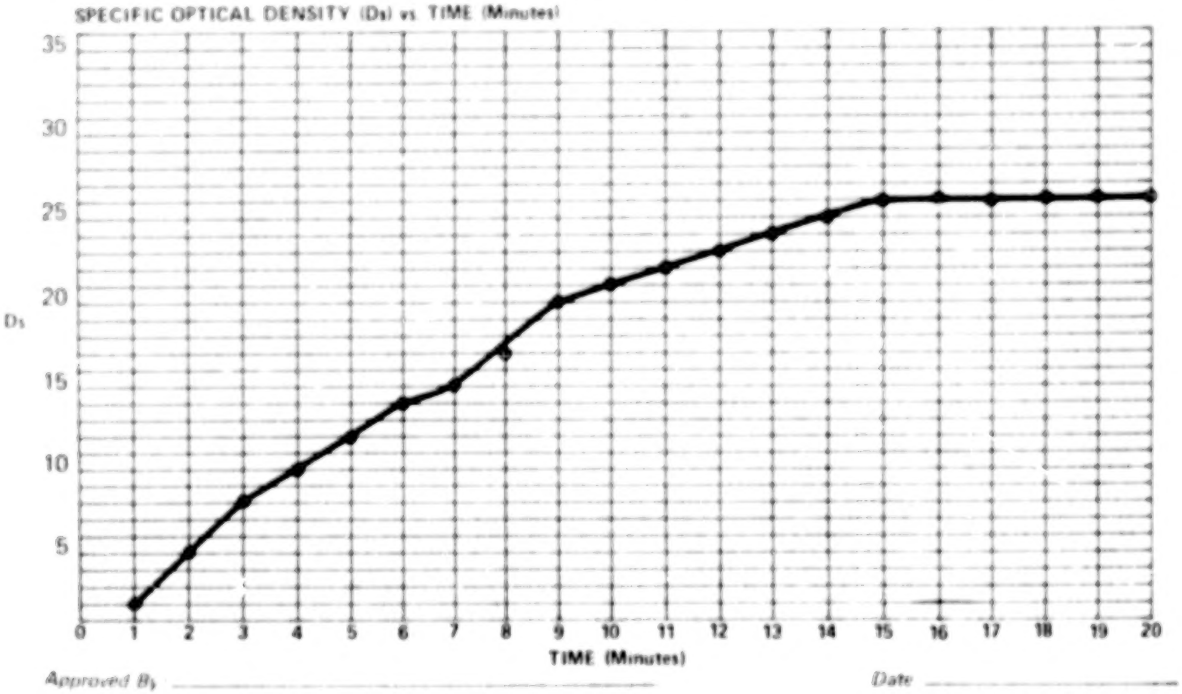
NBS SMOKE DENSITY MEASUREMENTS ON NCNS-12M/181E GLASS LAMINATE I-24A-95

Test Mode FLAMING

Submitted By: _____

SAMPLE LOG	1	2	3	Average
Time To Develop Ds = 100 (minutes)	N.A.			
Ds at 1.5 minutes	1			
Ds at 2.0 minutes	4			
Ds at 4.0 minutes	9			
Maximum Specific Optical Density, Dm (corr.)	21			

REMARKS: Flame @ 0.45 min. Buckling @ 0.70 min. Flame tips and sample flame extinguished due to small explosion of sample material @ 1.6 min. Gas and Air shut off. Radiant test mode continued to 20 min. mark. Ds = 16 @ 8.0 min.



Approved By _____

Date _____

FIGURE 22

SMOKE DENSITY TEST

REQ. No. 117H 68 1

Budget Ctr. RE 8060

Sample No. 122F 51

Date 12 1-77

Sample Description: NCNS 12M / HT S GRAPHITE FIBER LAMINATE.

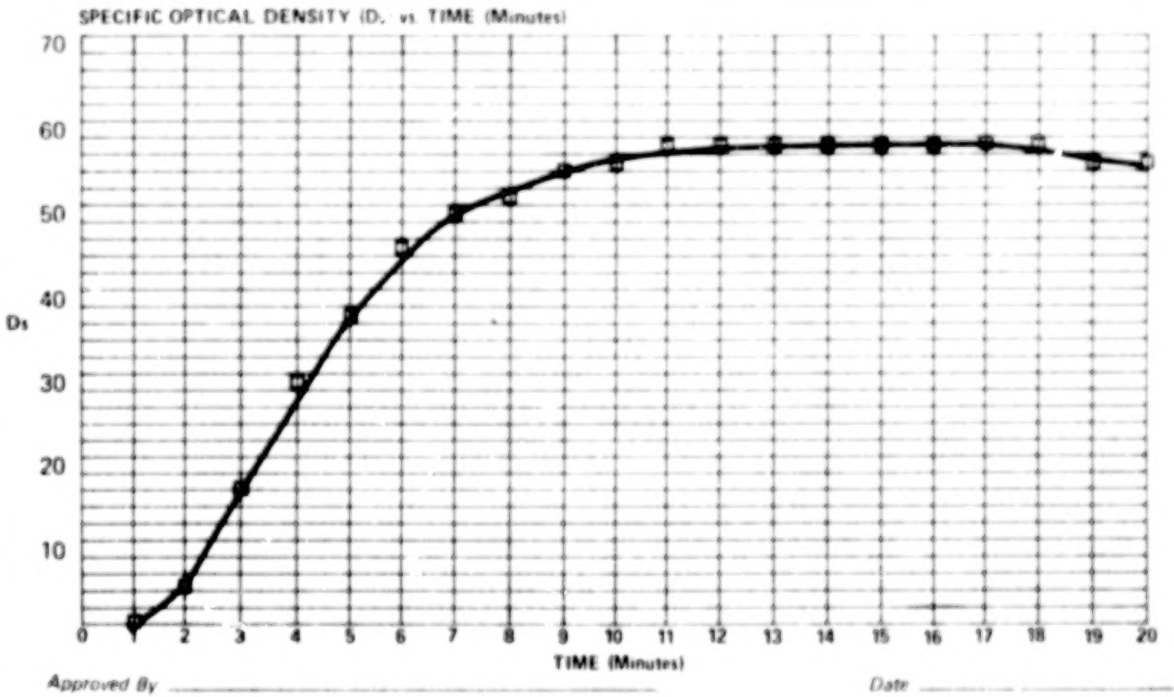
60% FIBER VOLUME

Test Mode FLAMING

Submitted By: FERRARA

SAMPLE LOG	1 ☐	2	3	Average
Time To Develop Ds = 100 (minutes)	*N.A.			
Ds at 1.5 minutes	1			
Ds at 2.0 minutes	4			
Ds at 4.0 minutes	29			
Maximum Specific Optical Density, Dm (corr.)	52			

REMARKS: ☐ *Not Applicable. Ignition @ 1.2 min. Flame out @ 7.25 min.



Approved By _____ Date _____

FIGURE 23

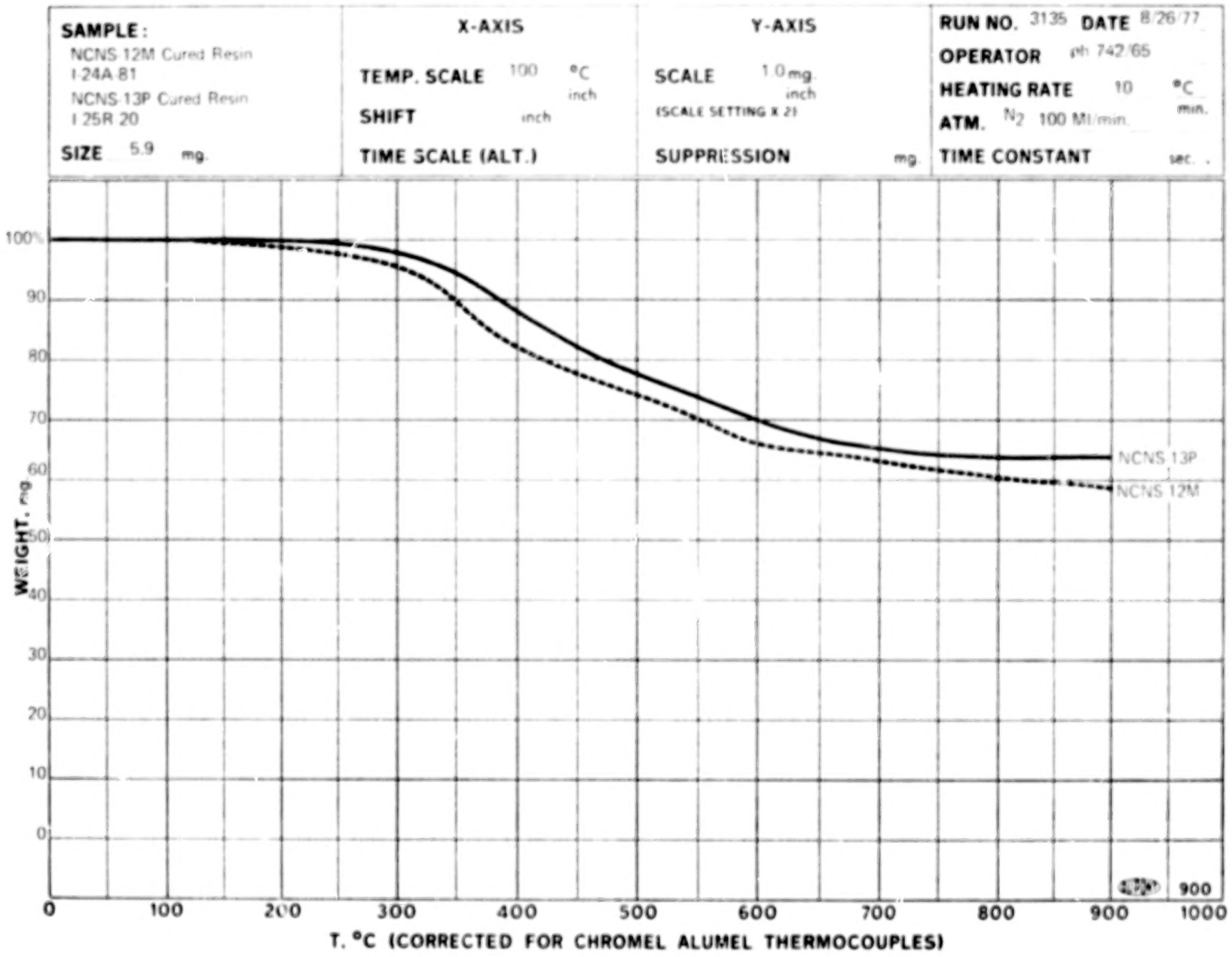


FIGURE 24 – THERMOGRAVIMETRIC ANALYSIS OF NCNS CURED RESINS

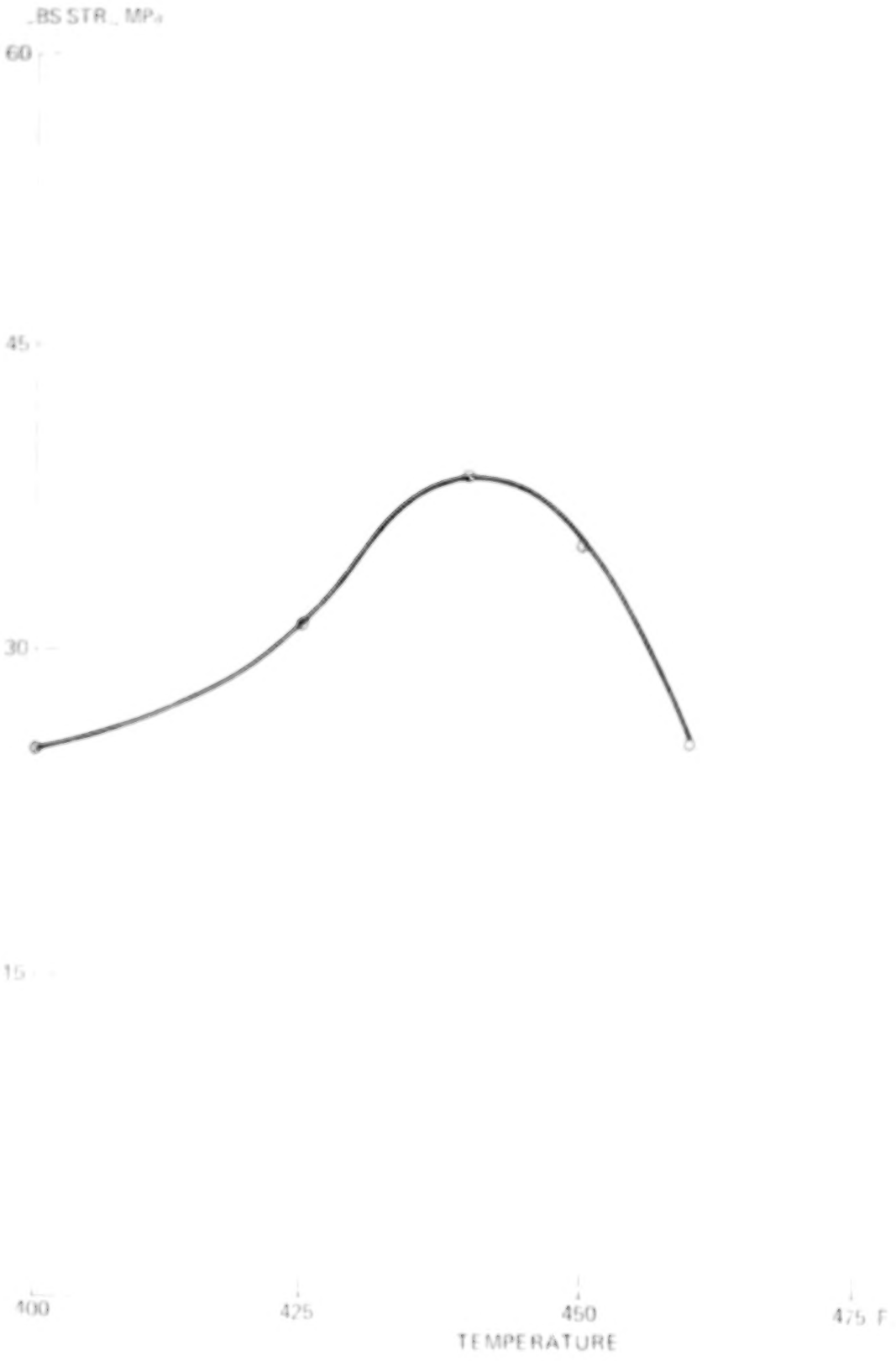


FIGURE 25 – NCNS 12M 181E GLASS FABRIC LAMINATE I 19N 139 POST CURING STUDIES

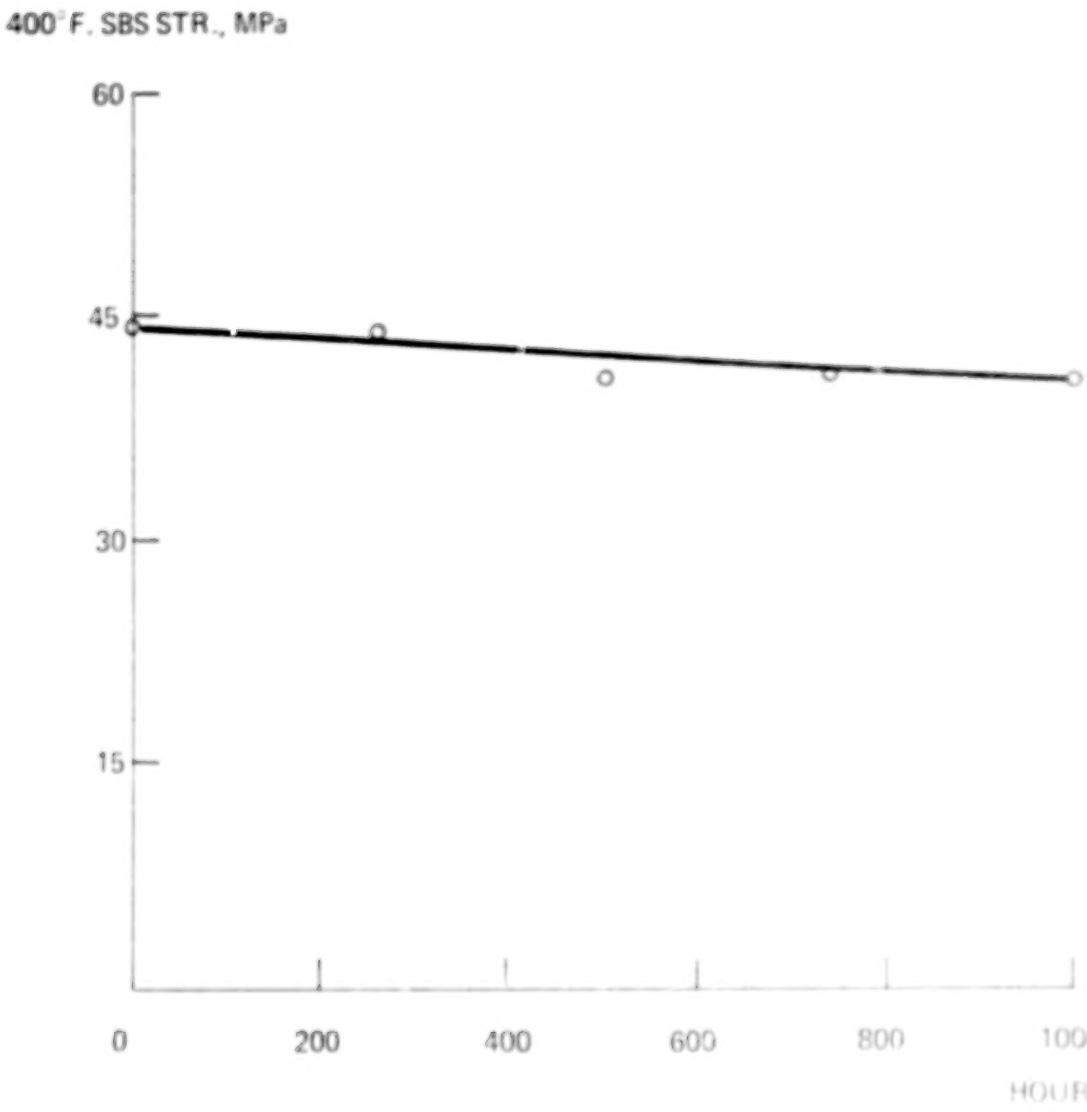


FIGURE 26 – 400° F. OXIDATIVE AGING OF NC-[illegible] 3M/181E GLASS LAMINATE [illegible] 16

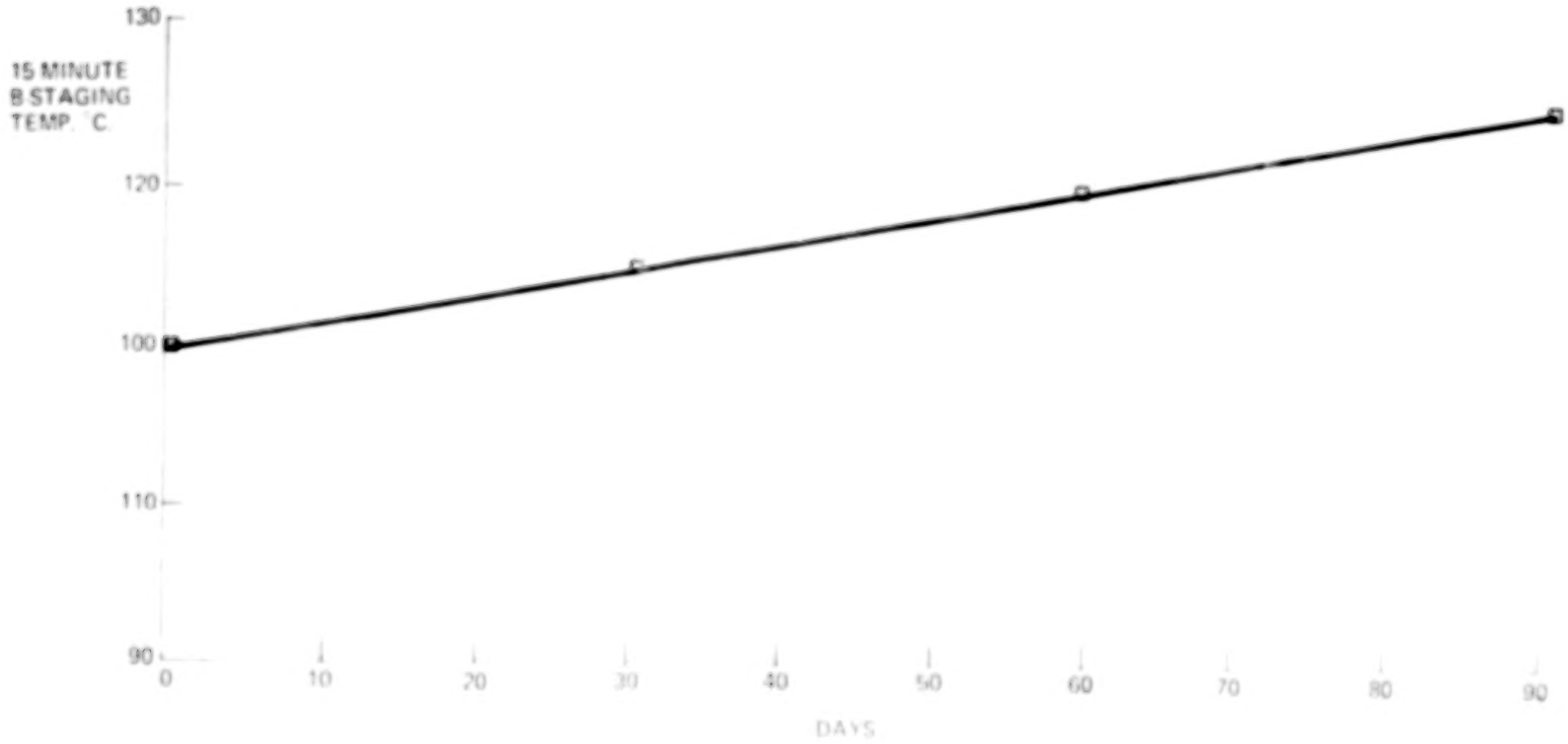


FIGURE 27 – ROOM TEMPERATURE STORAGE OF NCNS 12M 181E GLASS PREPREGS

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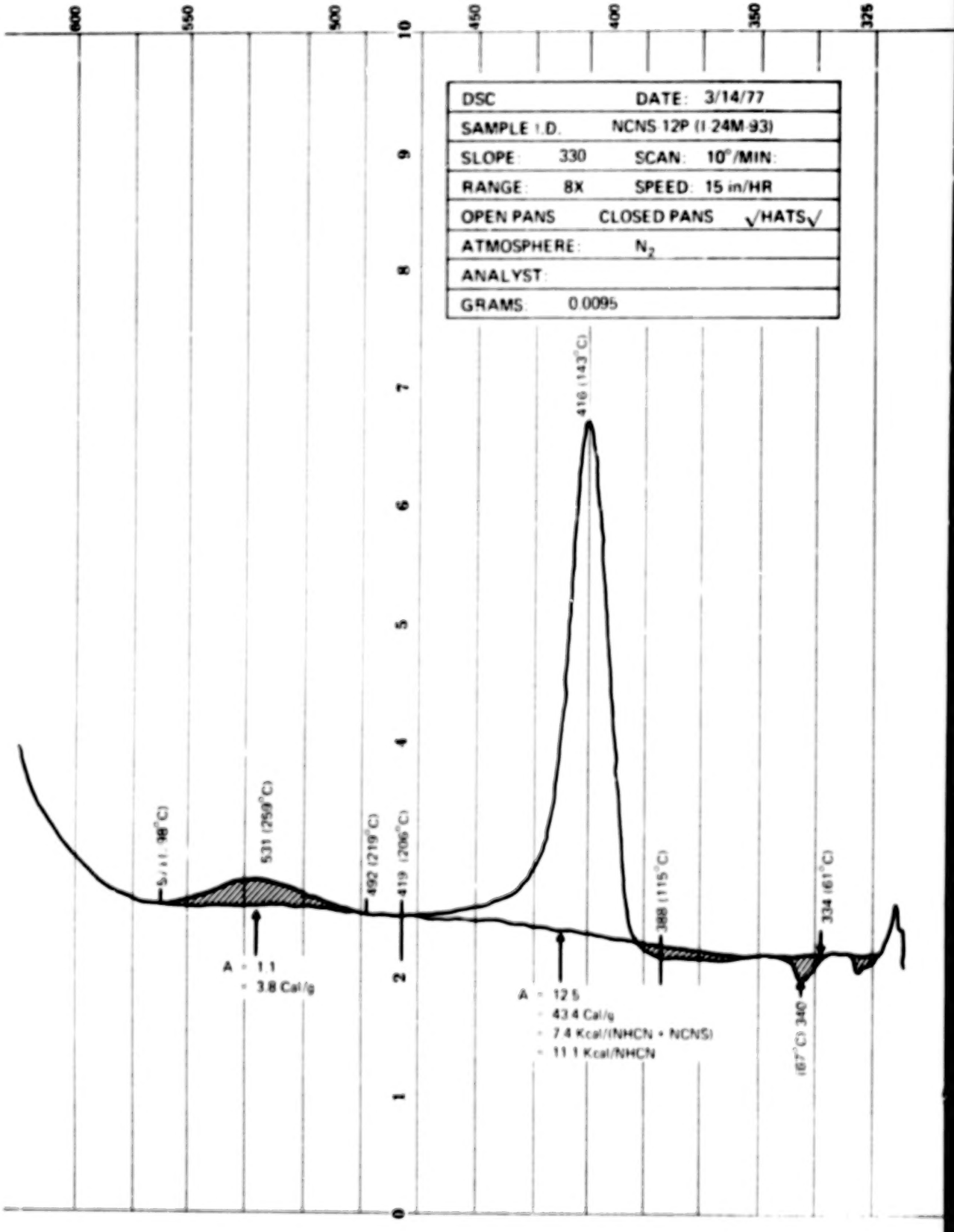


FIGURE 28 – DIFFERENTIAL SCANNING CALORIMETRY OF NCNS-12P RESIN-RUN No. I-24M-93

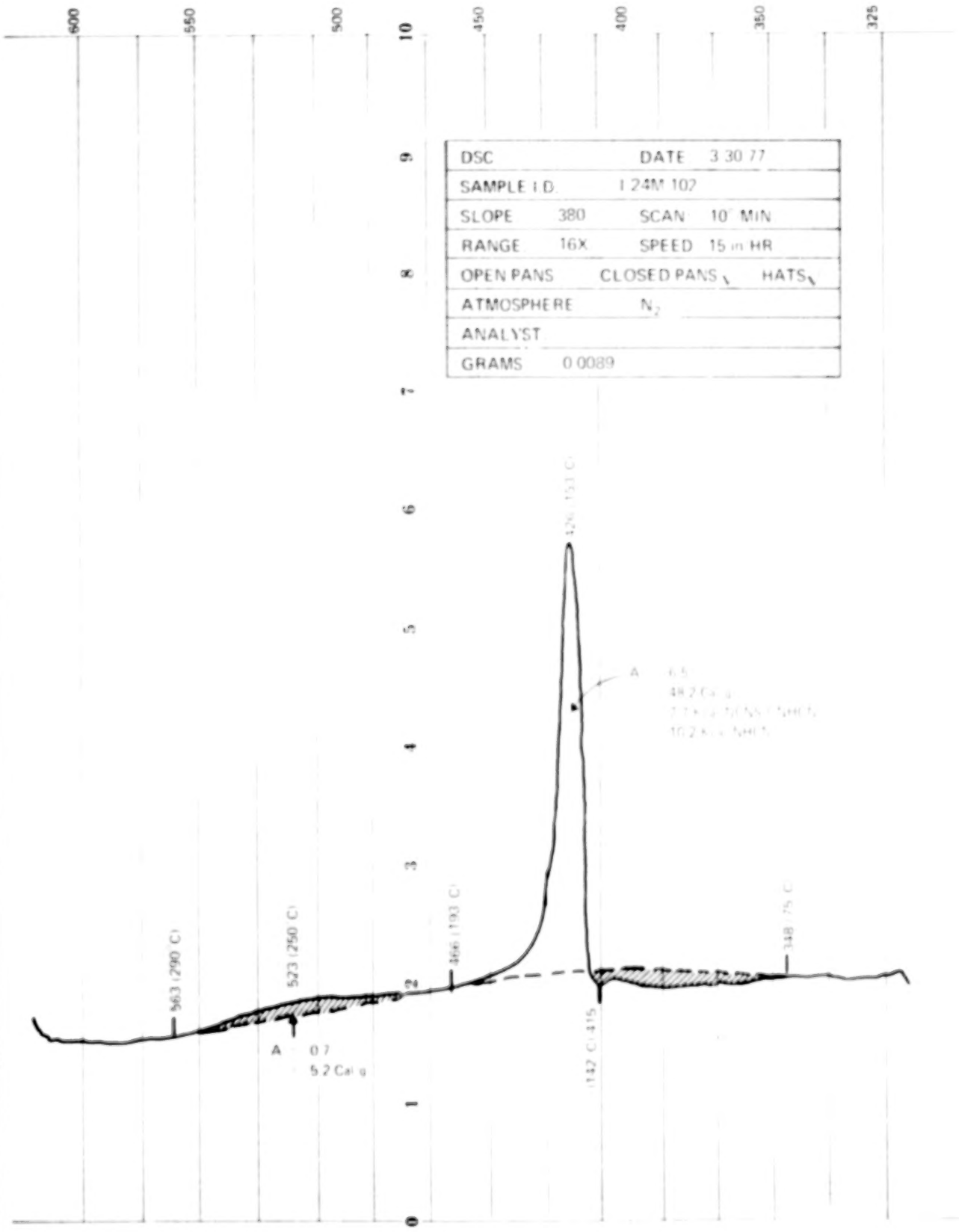


FIGURE 29 – DIFFERENTIAL SCANNING CALORIMETRY OF NCNS 13P
RUN No. I-24A-102

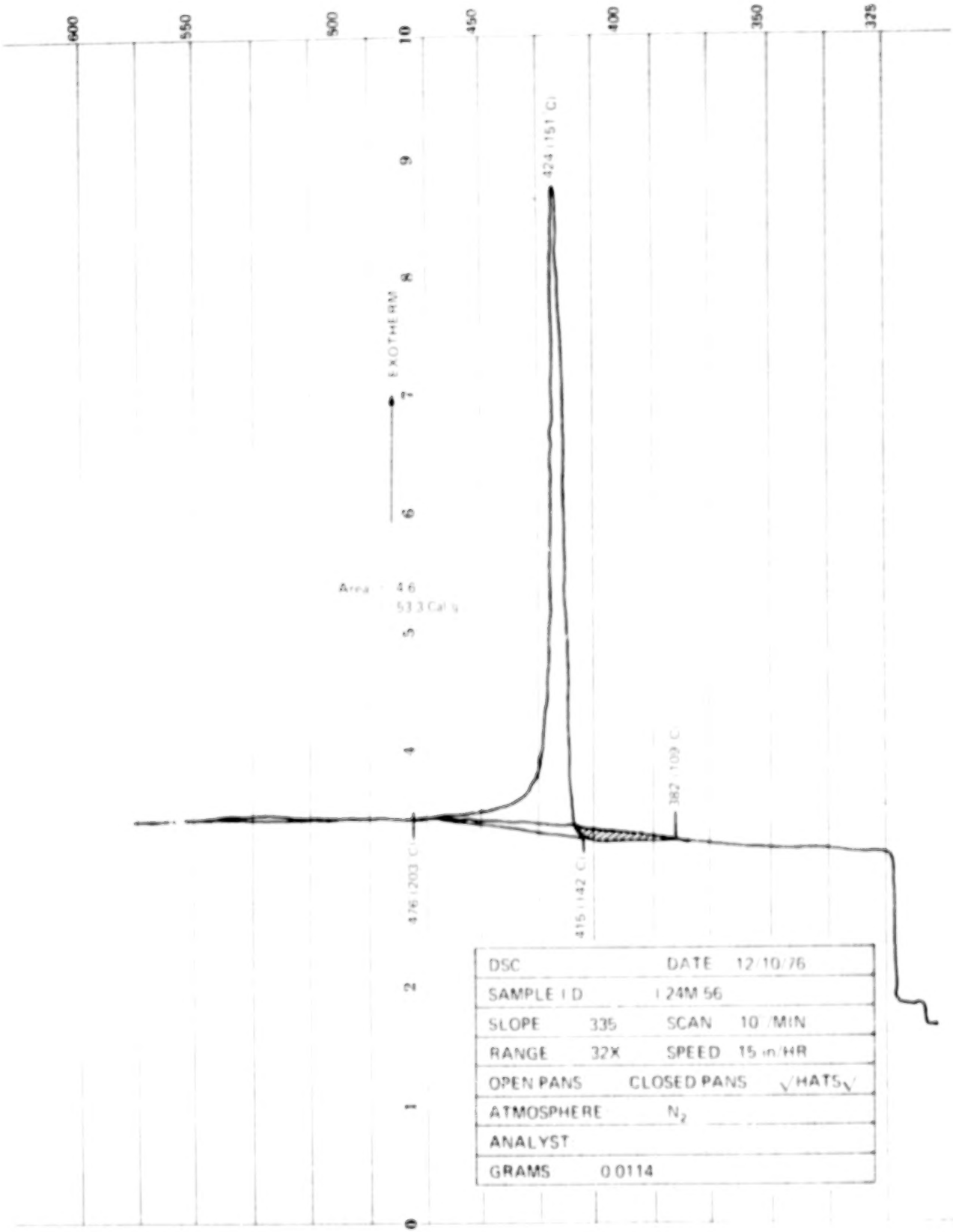


FIGURE 30 – DIFFERENTIAL SCANNING CALORIMETRY OF NCNS 14P RESIN RUN No. I-24M-56

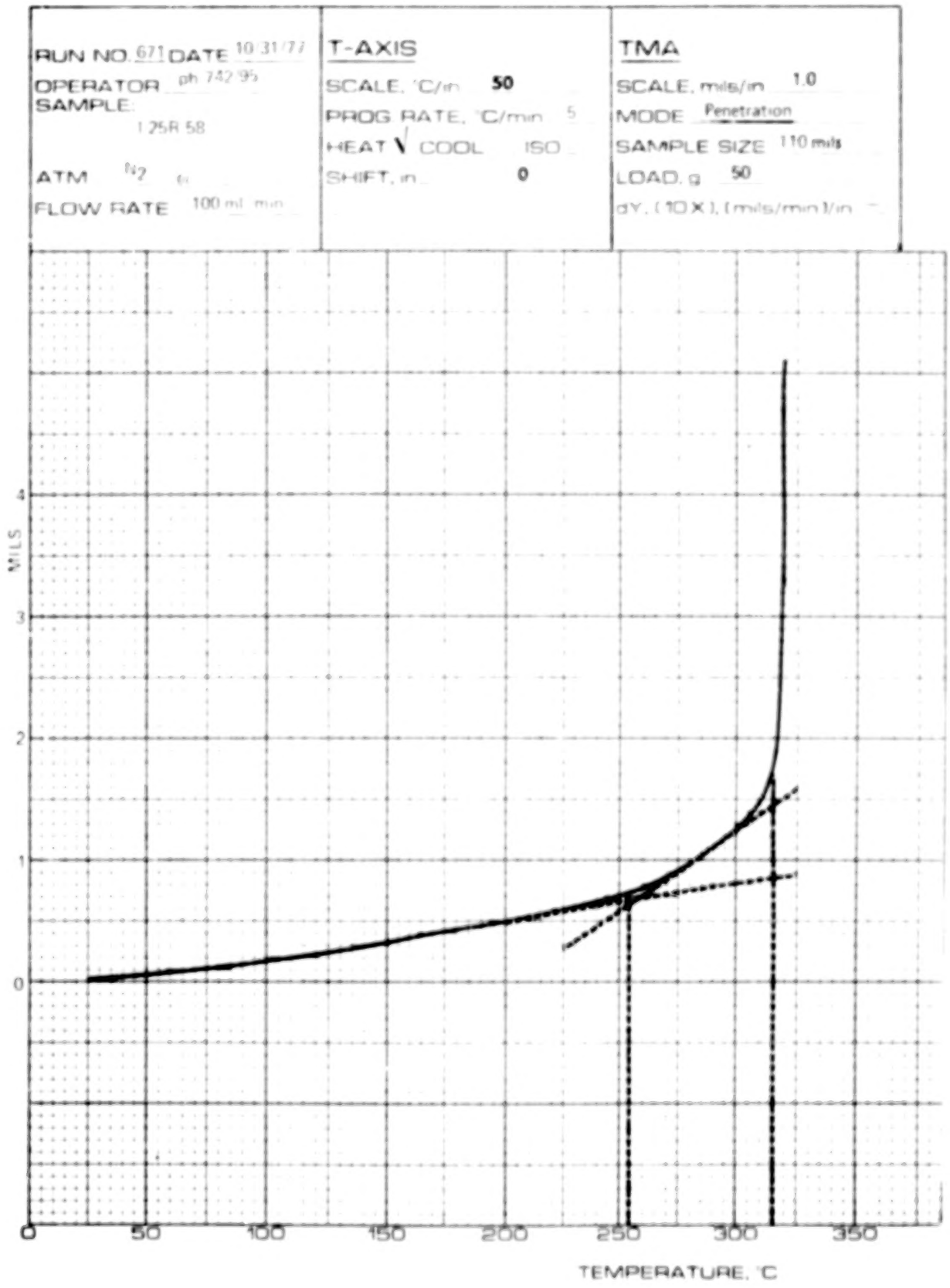


FIGURE 31 – Z-AXIS THERMAL EXPANSION OF NCNS 13P/181E GLASS CLOTH LAMINATE I 25R 58

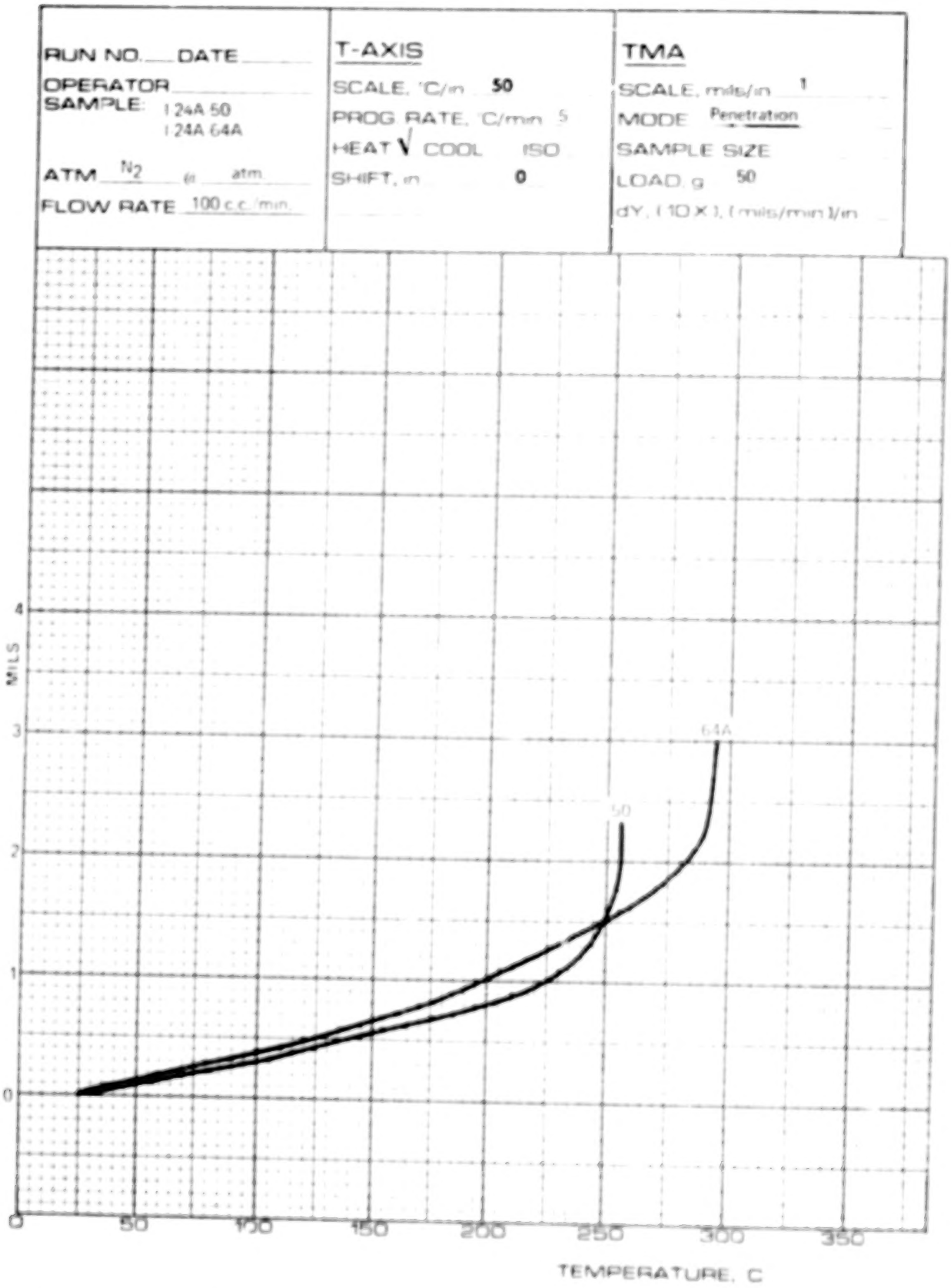


FIGURE 32 – THERMAL EXPANSION IN Z AXIS OF NCNS 12P AND NCNS 13P RESIN UNIDIRECTIONAL HT S GRAPHITE FIBER LAMINATES

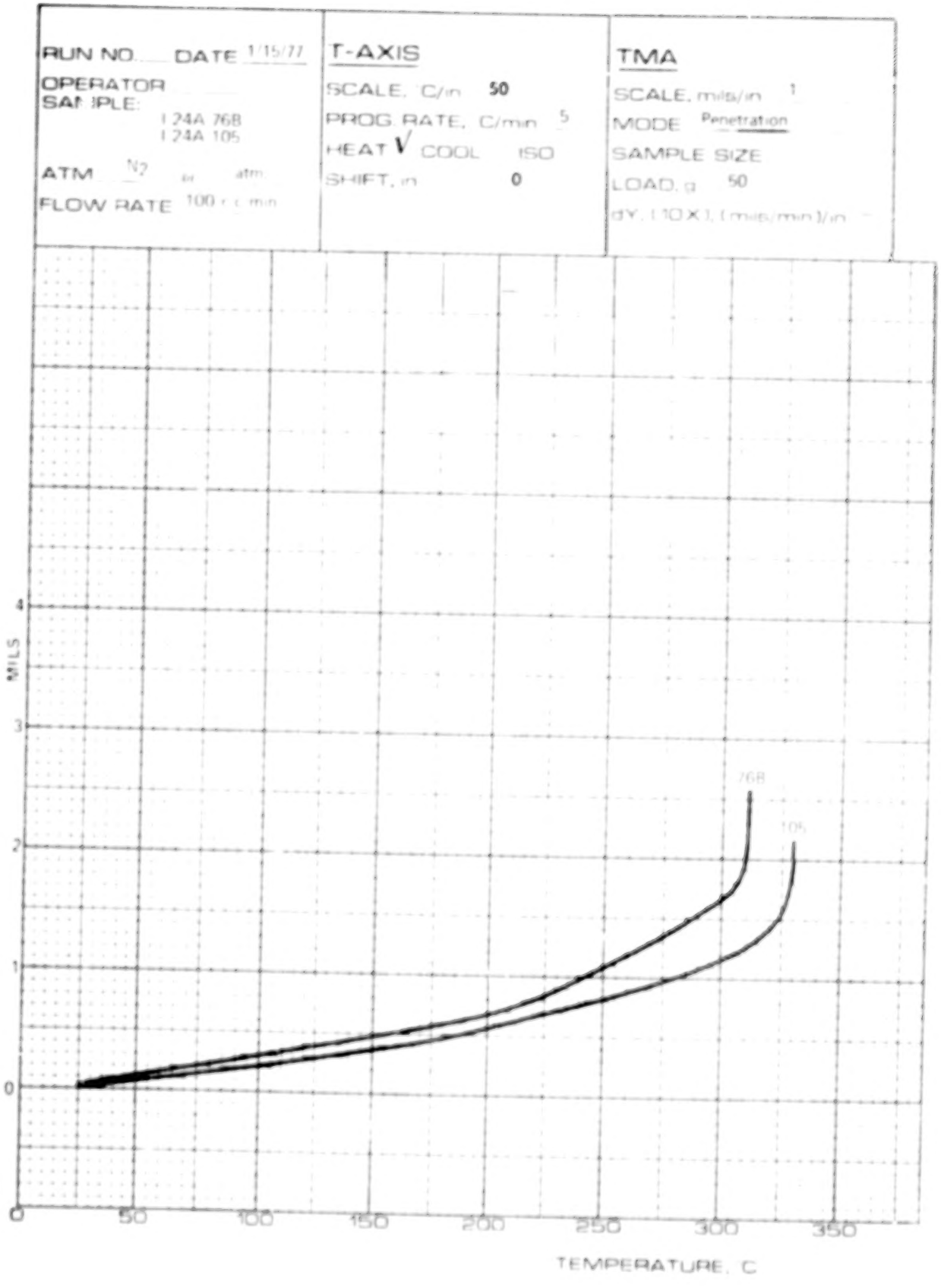


FIGURE 33 – EFFECT OF POST CURE CYCLE ON THERMAL EXPANSION IN Z AXIS OF NCNS 13P/HT S UNIDIRECTIONAL GRAPHITE FIBER LAMINATES

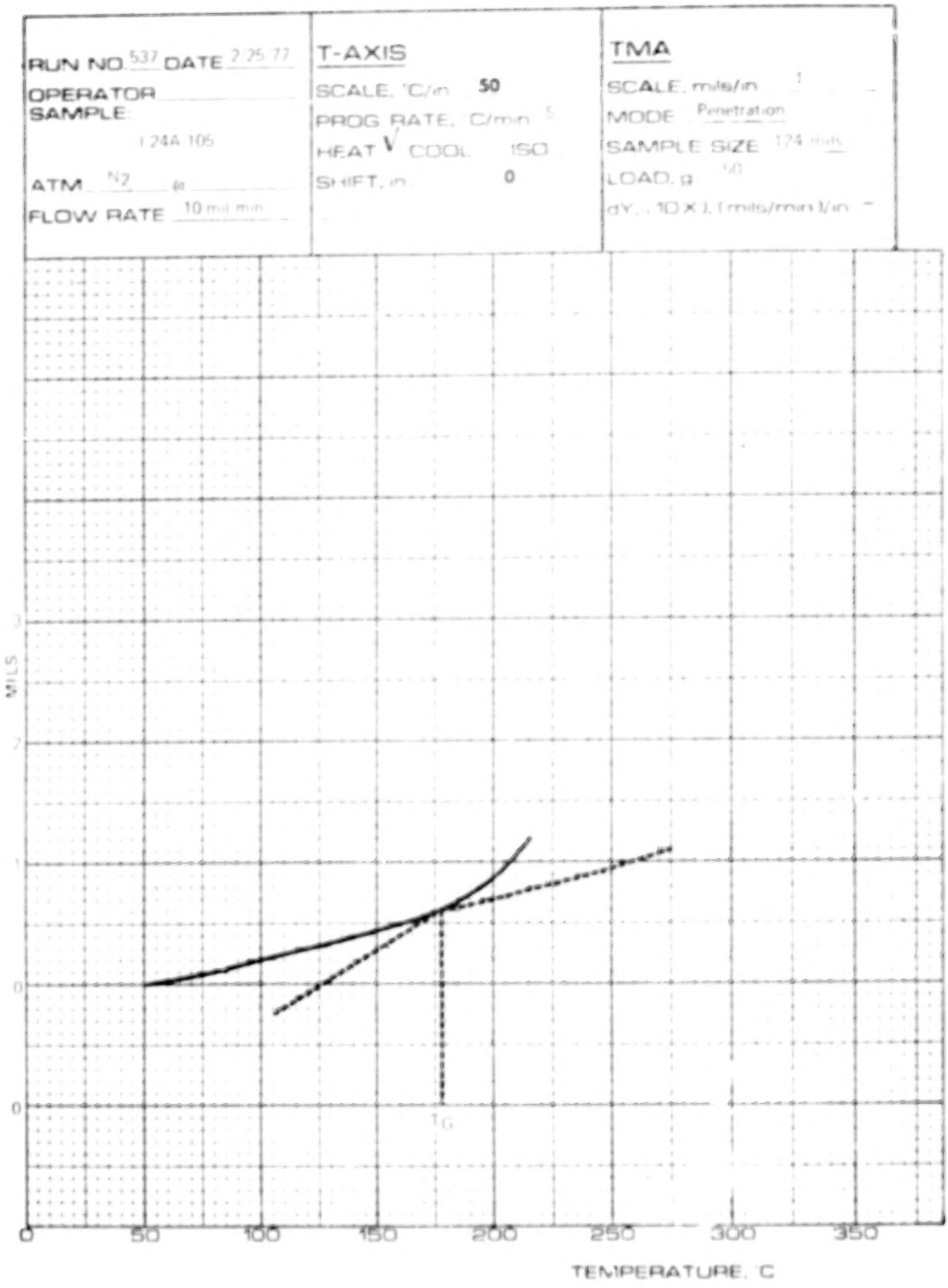


FIGURE 34 – Z AXIS THERMAL EXPANSION OF NCNS 13P/HT S GRAPHITE FIBER LAMINATE I 24A 105 AFTER 30 DAY, 95% R.H., 120° F, HUMIDITY EXPOSURE

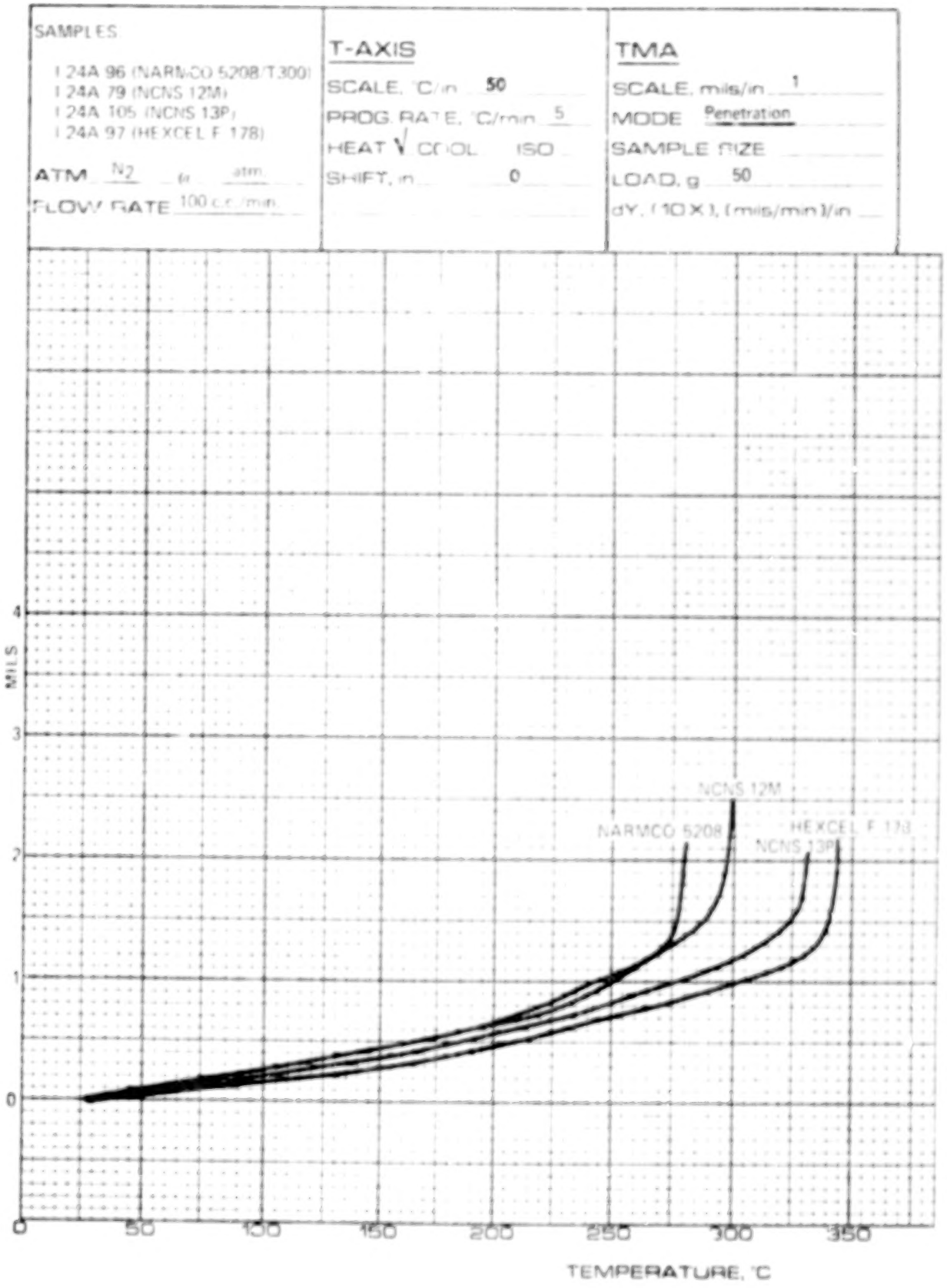


FIGURE 35 – COMPARISON OF THERMAL EXPANSION IN Z AXIS OF COMPETITIVE RESINS IN UNIDIRECTIONAL GRAPHITE FIBER LAMINATES

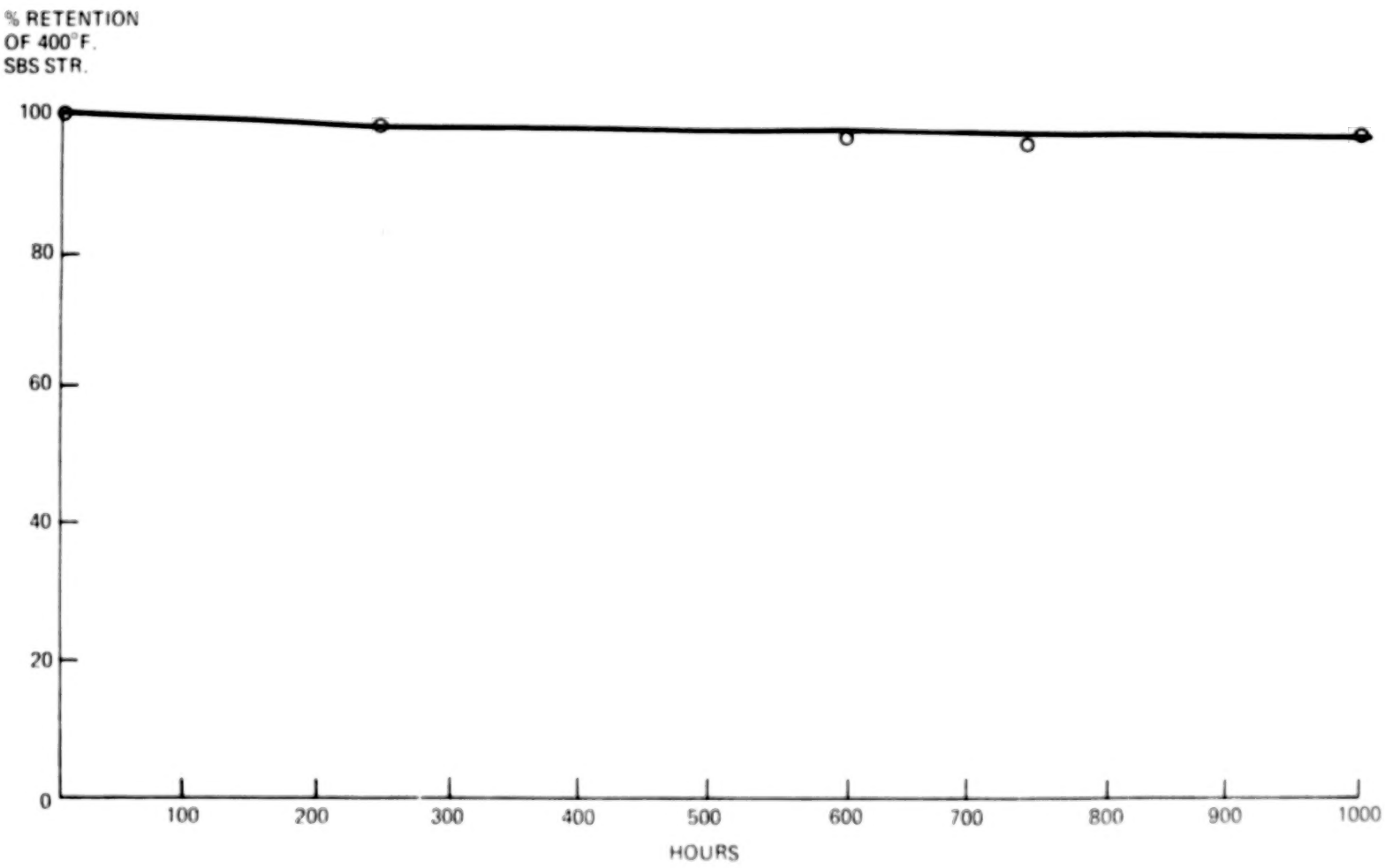


FIGURE 36 -- 400°F OXIDATIVE AGING OF NCNS-14P/HT-S UNDIRECTIONAL LAMINATE I-24A-103A

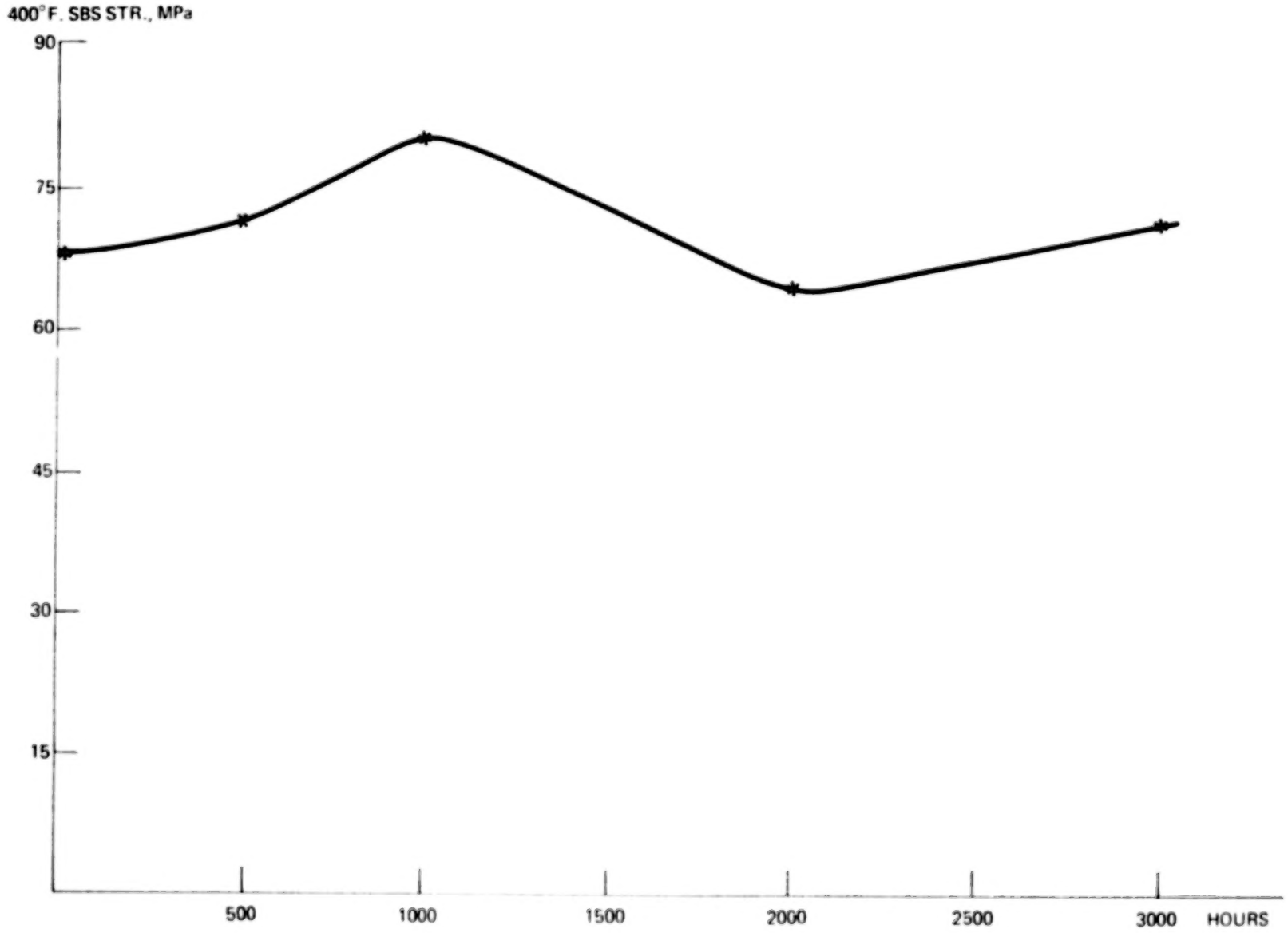


FIGURE 37 – 450°F. OXIDATIVE AGING OF NCNS-13P UNIDIRECTIONAL AS GRAPHITE FIBER LAMINATE I-25R-114

SMOKE DENSITY TEST

REQ. No. 117H-63 25

Budget Ctr. RE 8060

Date 9/29/77

Sample No.: 1-25R-26

Sample Description: NCNS 13P/181E Glass Cloth Laminate

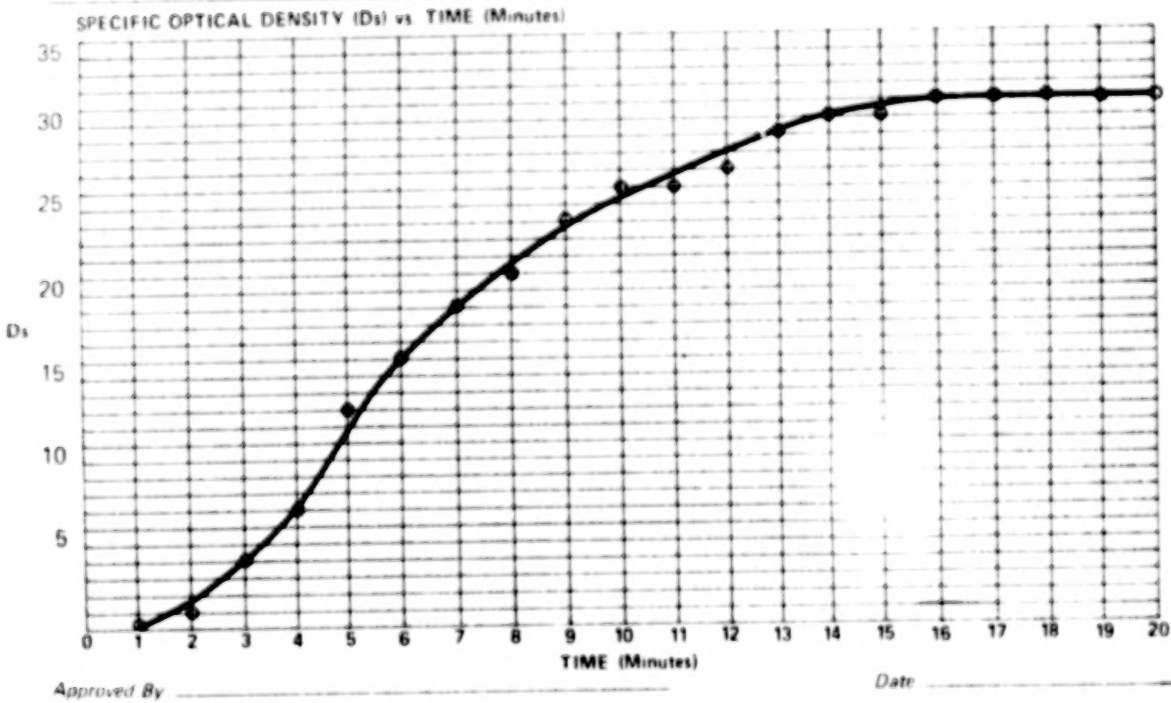
resin content 24.6%

Test Mode FLAMING

Submitted By

SAMPLE LOG	1	2	3	Average
Time To Develop Ds = 100 (minutes)				
Ds at 1.5 minutes	1			
Ds at 2.0 minutes	1			
Ds at 4.0 minutes	7			
Maximum Specific Optical Density, Dm (corr.)	29			

REMARKS Flame at 1.15 min. - Flame out at 2.6 min.



Approved By

Date

FIGURE 38

SMOKE DENSITY TEST

REQ. No. 117H-78-23

Budget Ctr. RE 7060

Sample No.: I-25R-114B

Date 3/30/78

Sample Description: NCNS 13P / Unidirectional AS graphite fiber laminate

– resin content 32.3%

Test Mode FLAMING

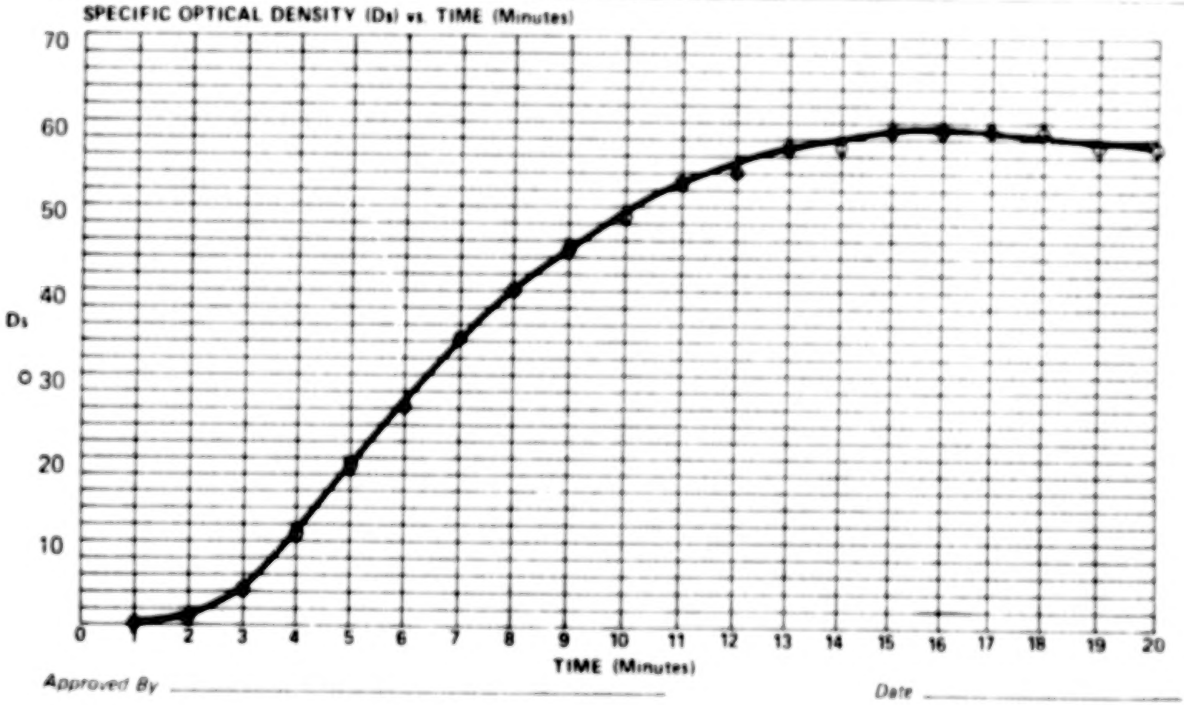
Submitted By: FERRARA / M.K.

SAMPLE LOG	1	2	3	Average
Time To Develop Ds = 100 (minutes)	#N.A.			
Ds at 1.5 minutes	0			
Ds at 2.0 minutes	1			
Ds at 4.0 minutes	11			
Maximum Specific Optical Density, Dm (corr.)	57			

REMARKS: Ignition @ 1.1 min.; Visible Smoke @ 1.7 min.; Flame out @ 6.75 min.

#N.A. = Not Applicable.

Weight Loss = 7.4%



Approved By _____ Date _____

FIGURE 39

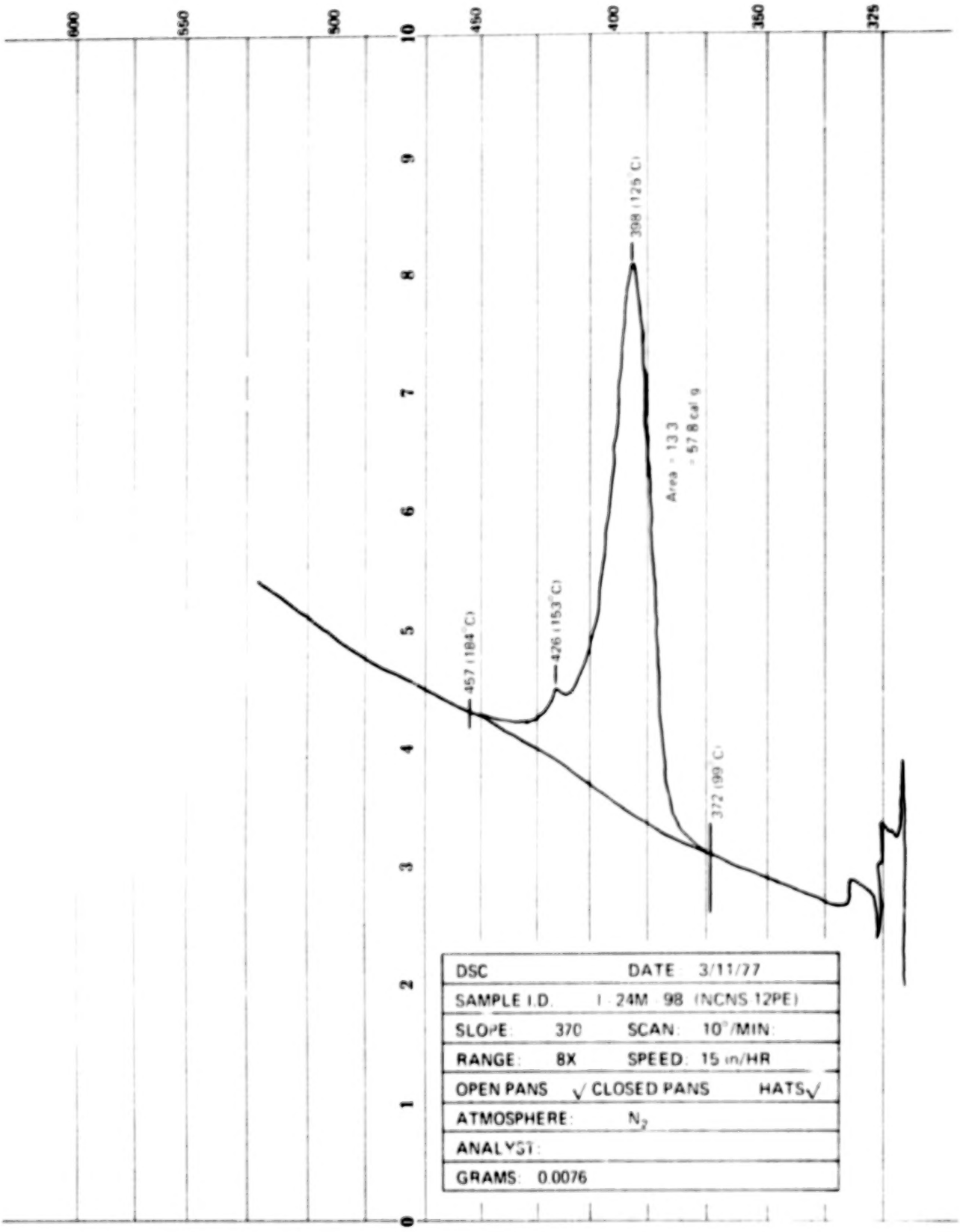


FIGURE 40 – DIFFERENTIAL SCANNING CALORIMETRY OF NCNS - 12PE RESIN RUN No. I-24M-98

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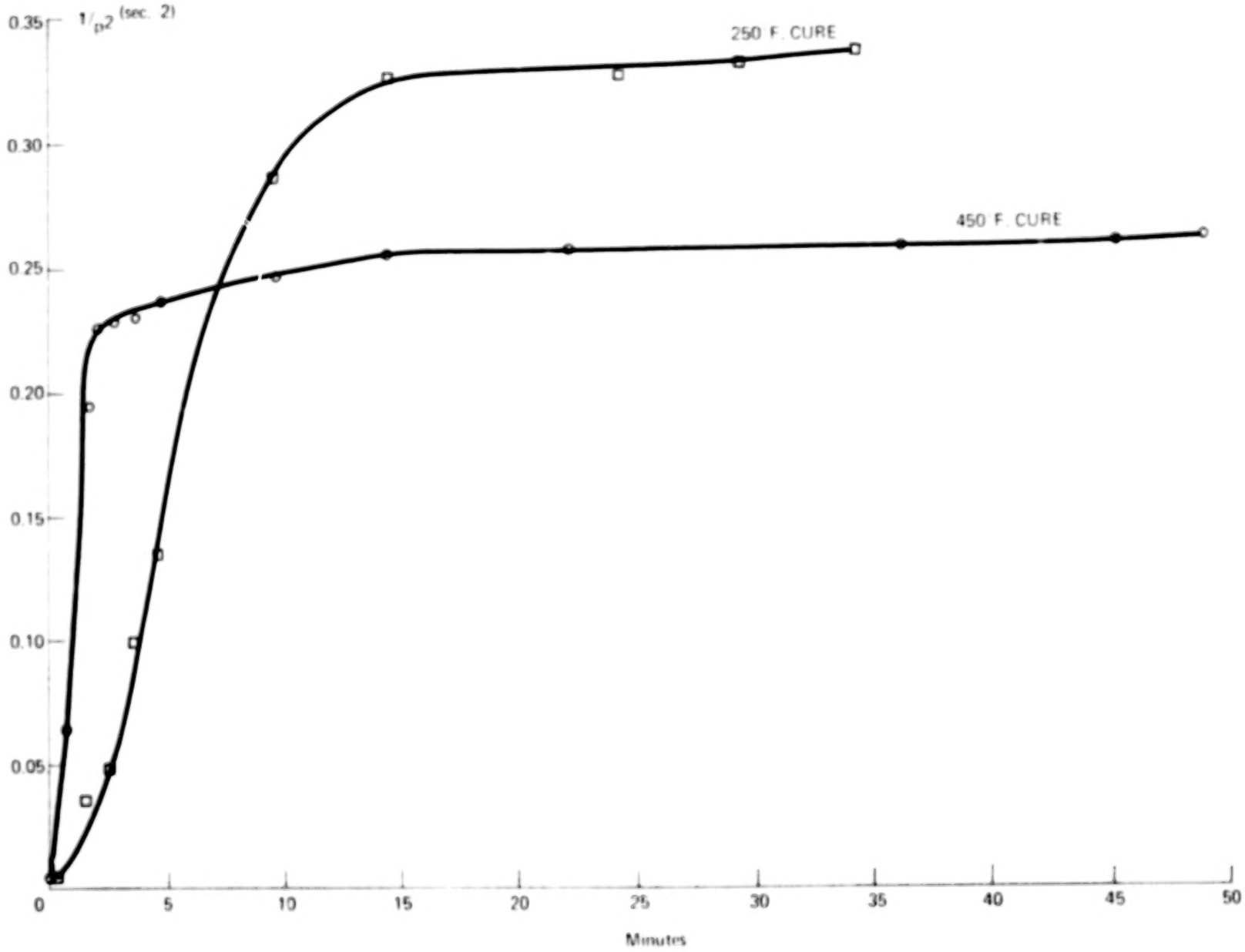

FIGURE 41 – RELATIVE MODULUS VS. TIME IN TORSIONAL BRAID CURING STUDY OF NCNS 13PE RESIN

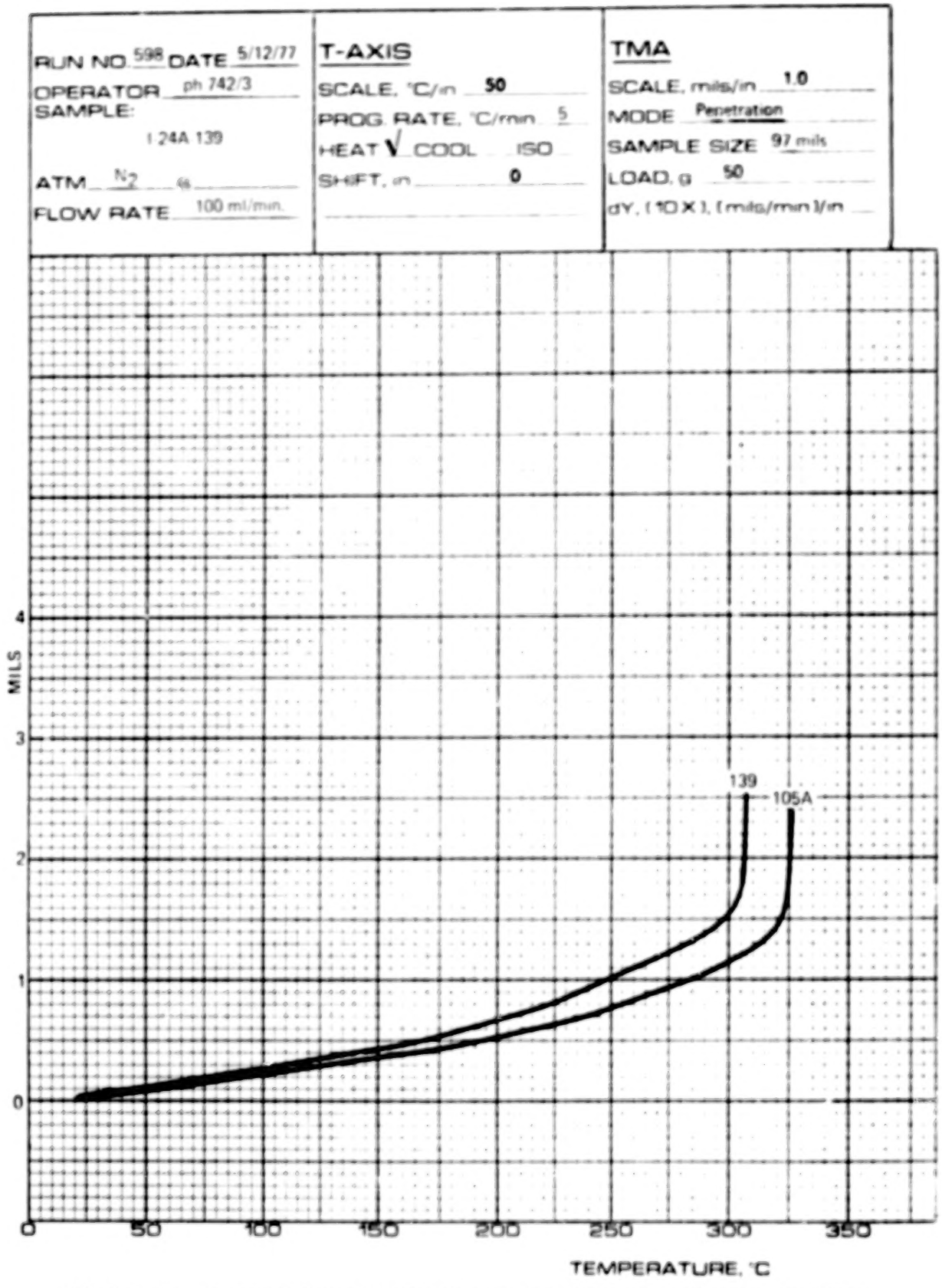

FIGURE 42 – Z-AXIS THERMAL EXPANSION COMPARISON OF NCNS-13PE/AS GRAPHITE FIBER LAMINATE I-24A-139 AND NCNS-13P/HT-S GRAPHITE FIBER LAMINATE I-24A-105A

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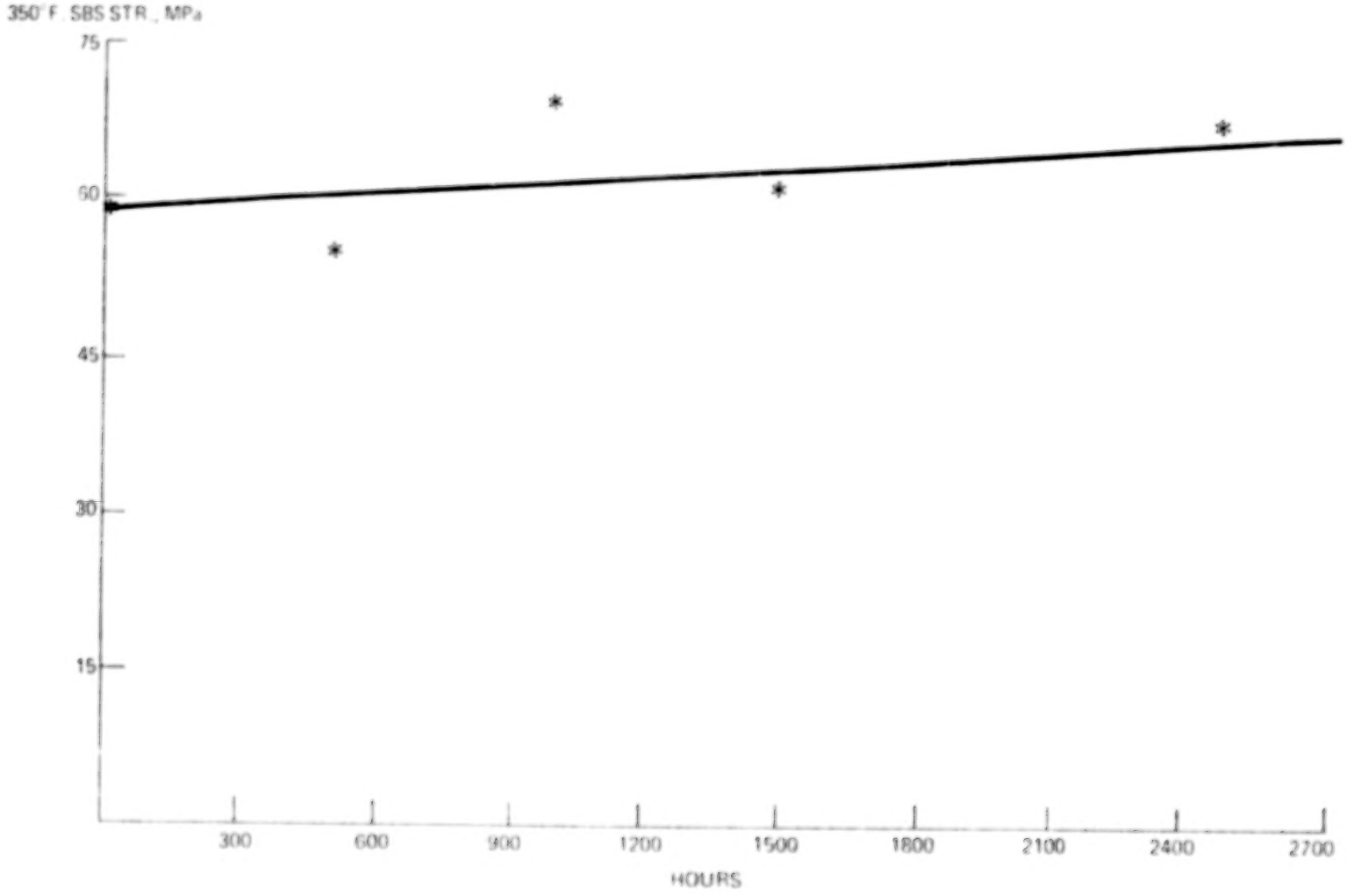

FIGURE 43 -- 350°F. OXIDATIVE AGING OF NCNS 13PE/UNIDIRECTIONAL GRAPHITE FIBER LAMINATE I-24A-139

SMOKE DENSITY TEST

REQ. No. 117H-60-1

Budget Ctr. RE 8060

Sample No.: I-25R-7A, I-25R-7B

Date 7-22-77

Sample Description:

NCNS 13PE/181E GLASS LAMINATES

Test Mode FLAMING

Submitted By: FERRARA

SAMPLE LOG	1	2	3	Average
Time To Develop Ds = 100 (minutes)	8.25	NA		
Ds at 1.5 minutes	0	0		
Ds at 2.0 minutes	2	1		
Ds at 4.0 minutes	40	27		
Maximum Specific Optical Density, Dm (corr.)	98	38		

REMARKS: Ignited @ 0.5 min. Flame out @ 2.5 min. Visible smoke @ 1.9 min. (I-25R-7A)

Ignited @ 0.25 min. Flame out @ 3.5 min. Visible smoke @ 1.0 min. (I-25R-7B)

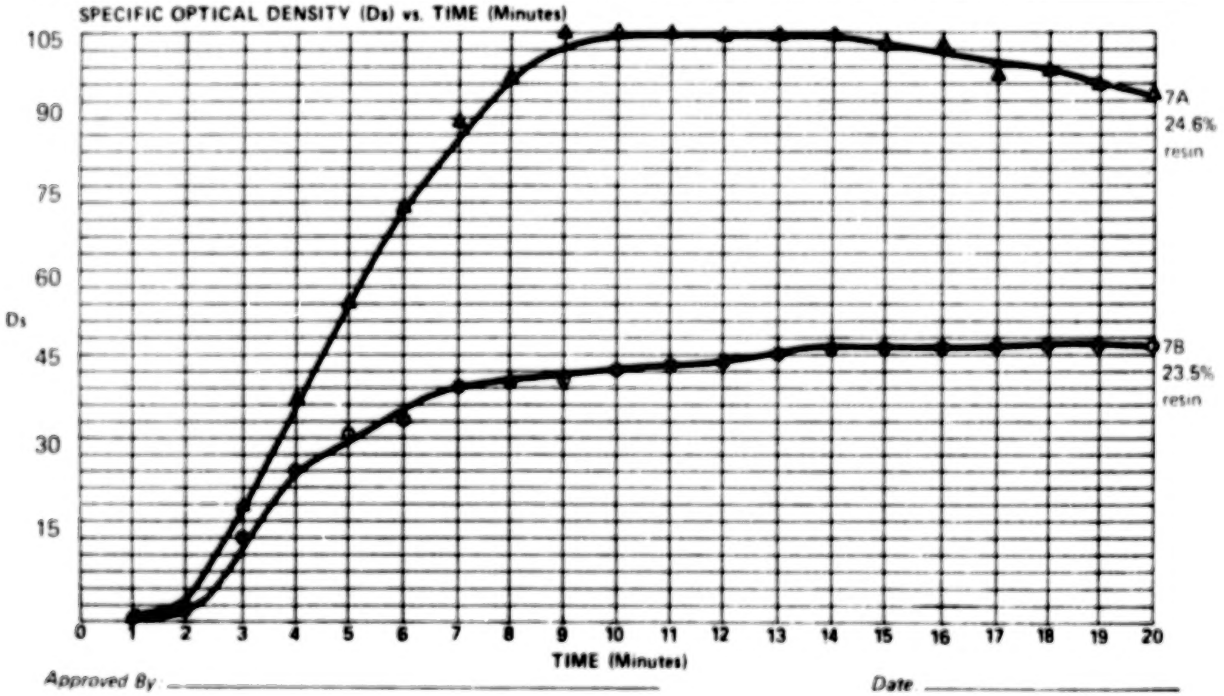

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FIGURE 44

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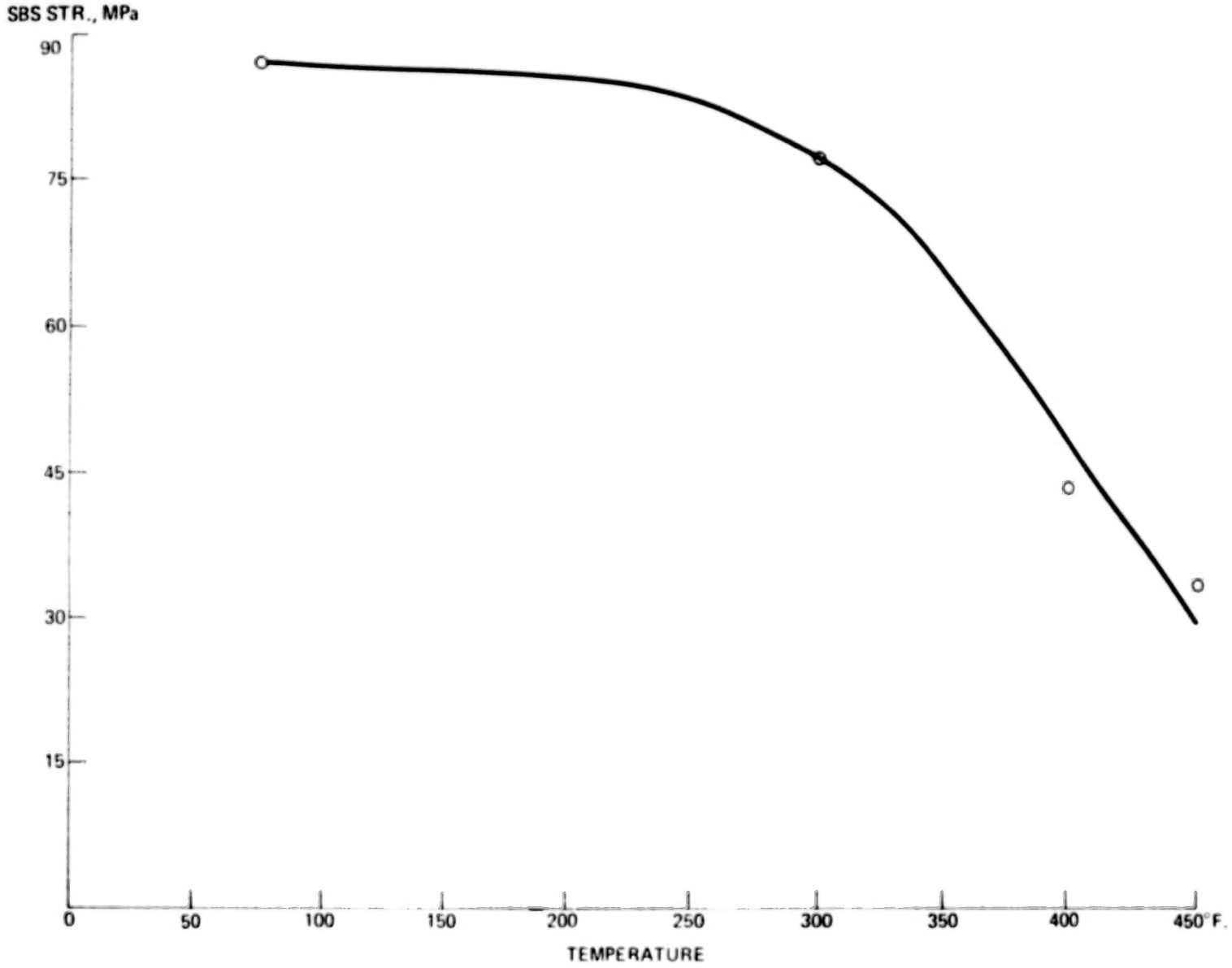

FIGURE 45 – INTERLAMINAR SHEAR STRENGTH VS TEMPERATURE OF NCNS-13PE/181E GLASS CLOTH LAMINATE I-25R-8A

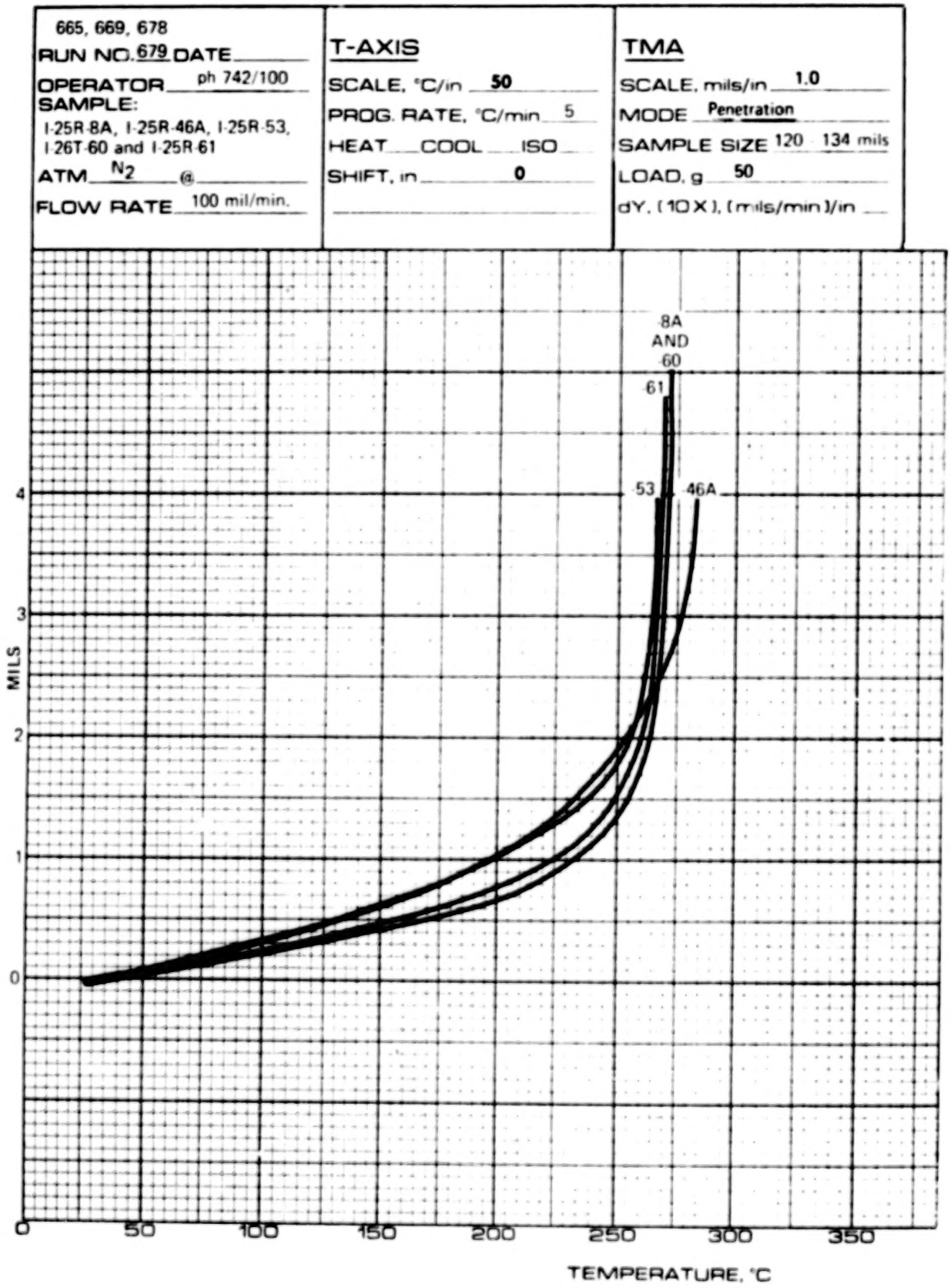

FIGURE 46 – Z-AXIS THERMAL EXPANSION OF 181E GLASS CLOTH LAMINATES PREPARED FROM NCNS-13PE RESINS I-25R-8A, I-25R-46A, I-25R-53, I-25R-60 AND I-25R-61

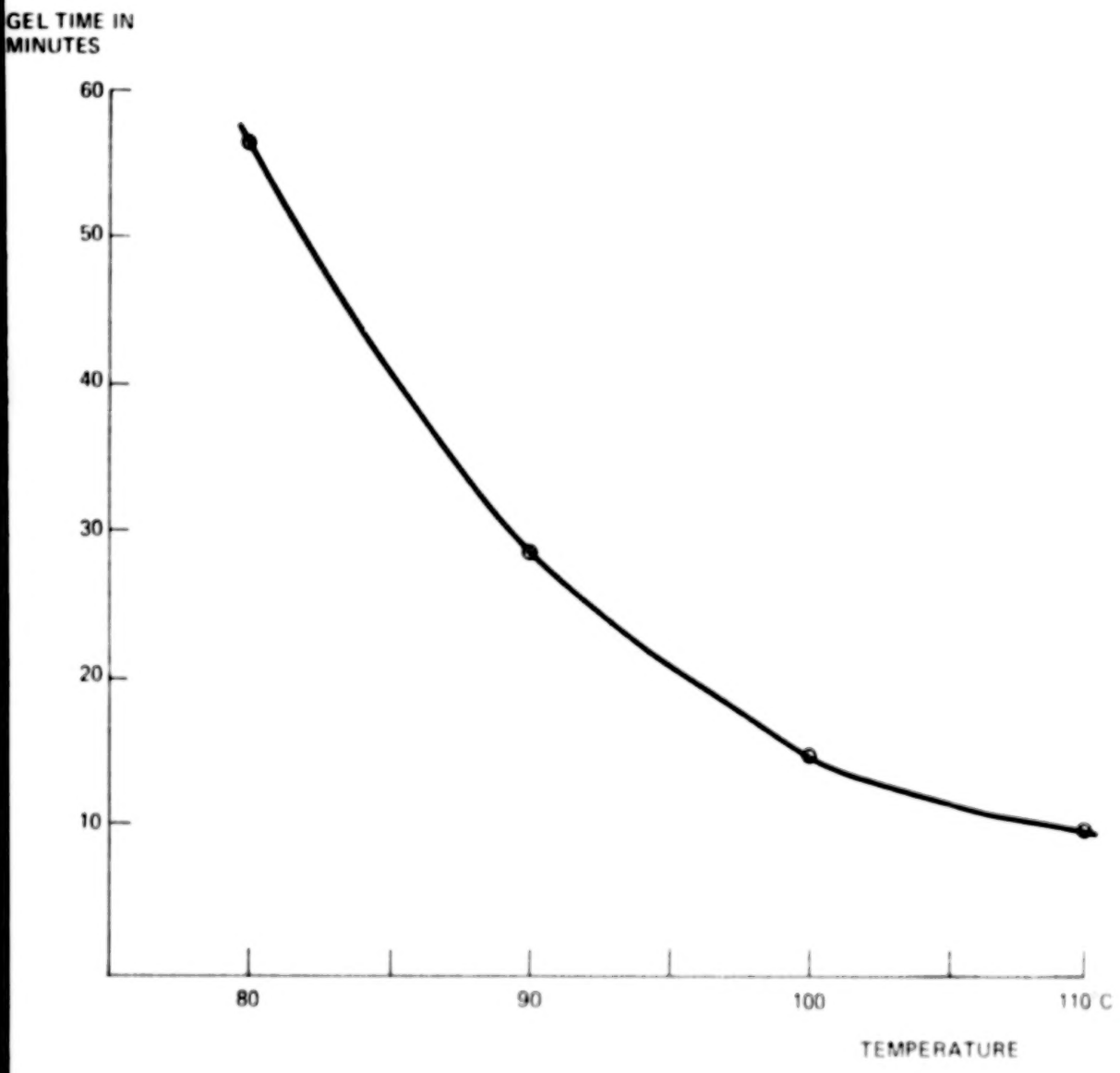

FIGURE 47 – GEL TIME VS. TEMPERATURE FOR 90/10 NCNS-13P/CY 179 RESIN BATCH NO. I-261-72

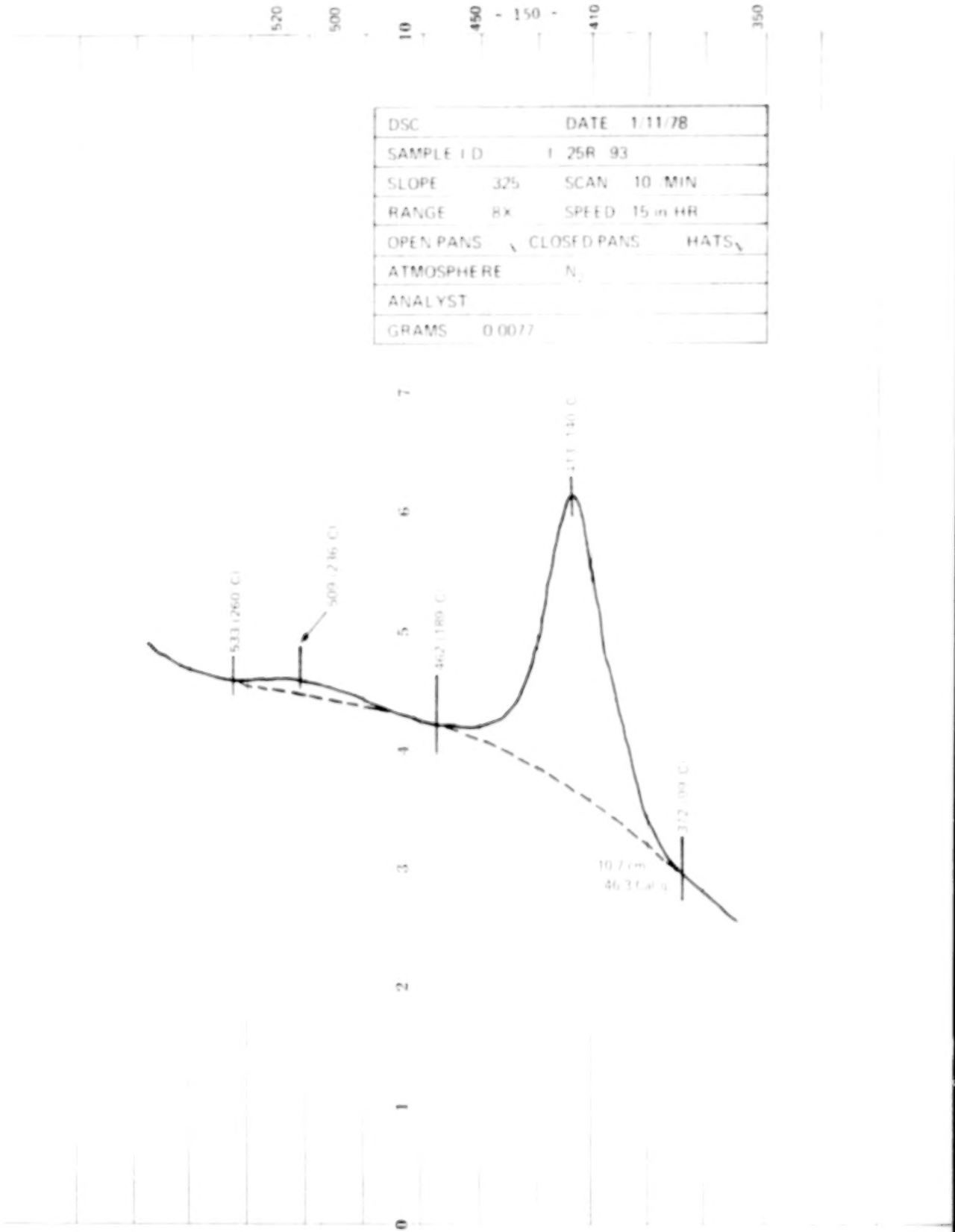

FIGURE 48 – DIFFERENTIAL SCANNING CALORIMETRY RUN ON 90% NCNS-13P/10% CY 179 EPOXY ALLOY

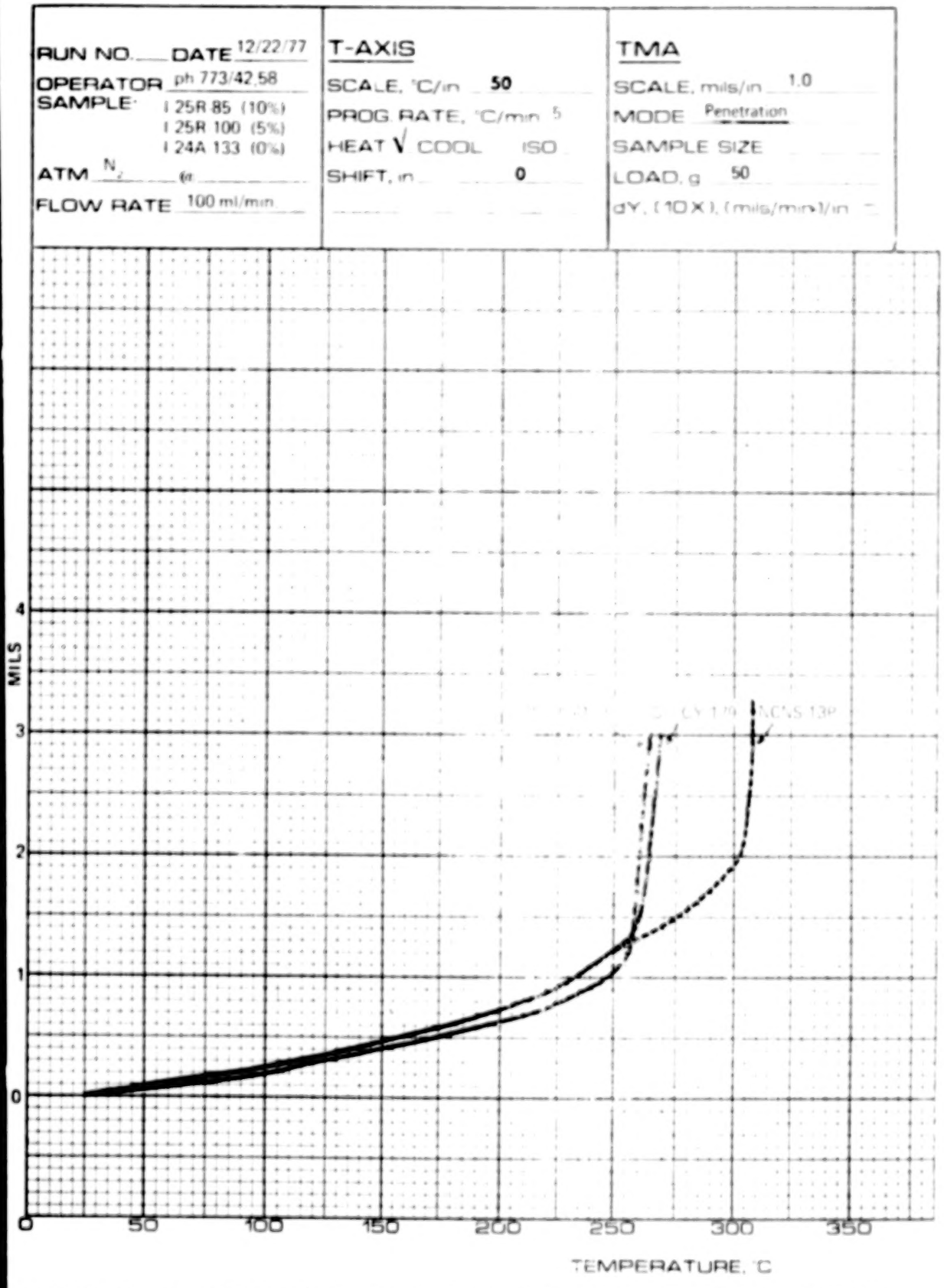

FIGURE 49 – Z-AXIS THERMAL EXPANSIONS OF AS UNIDIRECTIONAL GRAPHITE FIBER LAMINATES PREPARED FROM NCNS-13P RESIN WITH VARYING AMOUNTS OF ARALDITE CY179 EPOXY RESIN

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15 Supplementary Notes

Langley Technical Monitor: James B. Nelson
Selected temperature, pressure and linear dimension values are given in U. S. Customary units.

16 Abstract

The objective of this program was to investigate and develop the most promising of a number of new addition-type polyimides and polyaromatic melamine (NCNS) resins for use in high performance composite materials. Three different cure temperature ranges were of interest: 530-560K (500-550°F), 475-530K (400-500°F), and 450K (350°F). Examined were a wide variety of polyimide precursors terminated with 5-norbornene groups and addition polymerized at 560K similar to PMR-15 and LARC-160 polyimides. In addition, a number of lower curing cinnamal end-capped polyimides and a bis-maleimide were investigated but were not found promising. A group of NCNS resins were investigated and some were found to be superior to current epoxy resins in moisture resistance, oxidative aging and flame and smoke properties.

17 Key Words (Suggested by Author(s))	18 Distribution Statement
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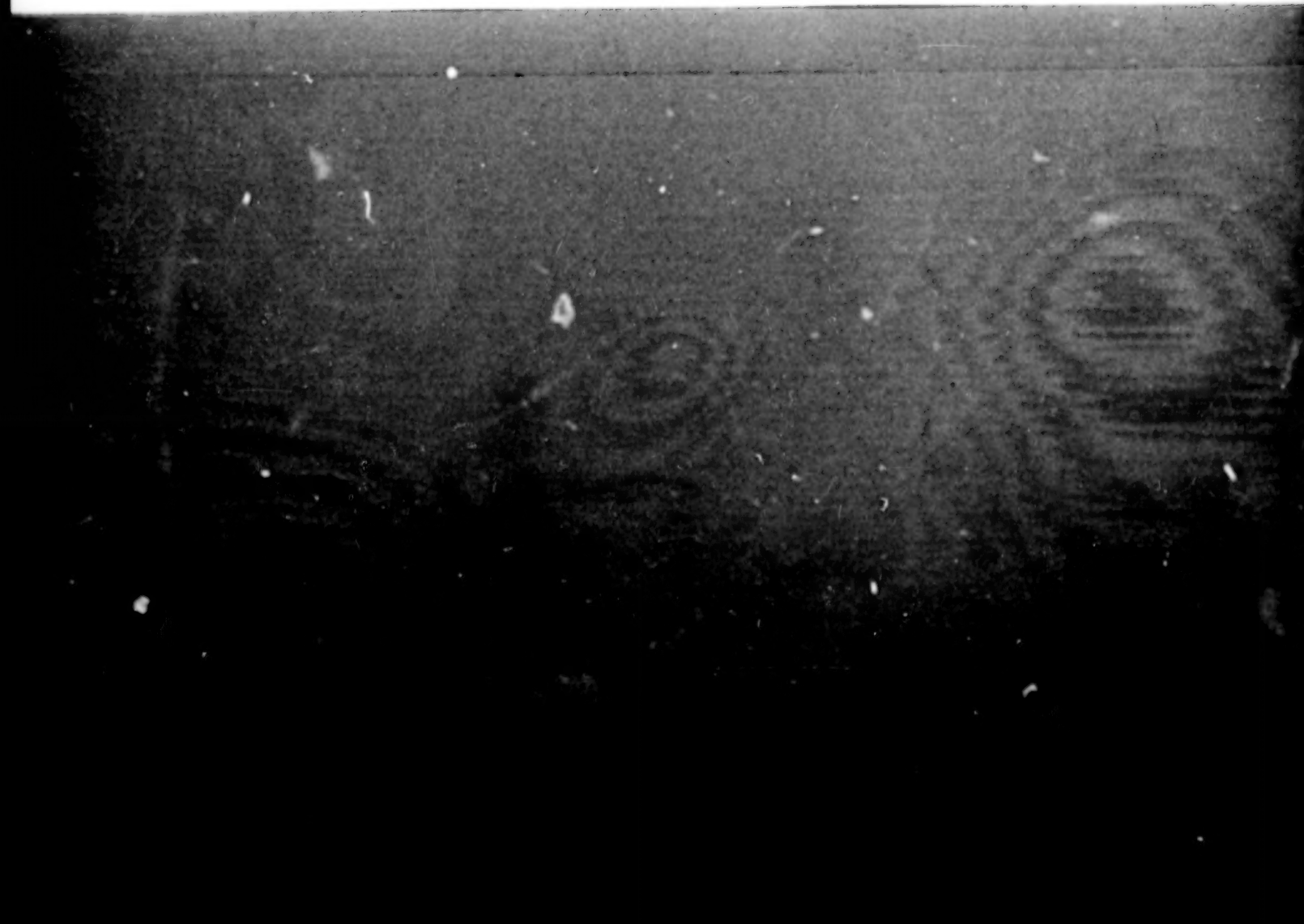

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